MINERAL MATTER IN COALS OF THE WEST COAST, SOUTH ISLAND, NEW ZEALAND

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CONTENTS

CHAPTER PAGE

CHAPTER PAGE

CHAPTER PAGE

FIGURES

FIGURE PAGE

FIGURE PAGE

FIGURE PAGE

FIGURE PAGE

TABLES

TABLE PAGE

ABSTRACT

Coals of the West Coast region (South Island, New Zealand) have been investigated by ash constituents analysis and X-ray diffraction of low temperature ash. Combined results from these techniques, together with evidence from sink-float fractions and inter-element relationships, are used to determine the mode of occurrence of major elements, strontium, barium, and nickel. Derivation of formulae for calculating mineral abundance allows the coals to be compared on a statistical basis.

A wide variation in mineralogical character is demonstrated for bituminous coals, particularly the highly diverse marginal marine Brunner coals (Paleocene-Eocene). Coals from the non-marine Paparoa Coal Measures (Late Cretaceous to Paleocene) are relatively uniform.

Mineral assemblages in Paparoa coals are variously dominated by kaolinite, quartz, illite, or siderite, and accompanied by minor proportions of crandallite, rutile and calcite. Deep circulation of groundwater from overlying marine rocks has locally altered siderite to pyrite. The relative abundance of detrital and syngenetic minerals, and distribution of minor ash constituents, is principally controlled by depositional environment and swamp character; differences in source rock composition appear to be of secondary importance. Mineralogical and chemical distinctions can be recognised for samples which have a contrasting coal type. Coals which have been attributed on petrographic evidence to relatively low water table swamps generally contain a highly kaolinitic mineral assemblage, which has resulted from periodic leaching of detrital minerals. Samples from swamps where a high water table is inferred contain abundant quartz, which originated from rafted vegetation.

Distribution of titanium and phosphorus minerals within seams of the Paparoa Coal Measures is complex. Sporadic crandallite-rich horizons are attributed to interaction of minerotrophic and leaching effects, whereby phosphate in the peat reacted with Al^{3+}. Maximum titanium concentrations commonly coincide with abundant crandallite, but the cause of this association is uncertain.

Siderite abundance appears to be controlled by permeability of the coal measure sediments.

Bituminous coals of the Brunner Coal Measures exhibit substantial variation in mineralogical composition as a result of differing depositional settings. In comparison to the Paparoa seams, Brunner coals lack

siderite, but contain locally abundant pyrite, dolomite, and boehmite. Slow and stable peat accumulation and isolation from sediment supply have resulted in some low ash coals, in which the mineral matter often shows mineralogical and chemical evidence of strong leaching of detrital sediment within the peat. In highly acid environments, both silica and alumina are believed to have been mobilised, yielding ultra-low ash coals. Where moderately acid conditions prevailed, decomposition of kaolinite and loss of silica has given rise to abundant boehmite. Boehmite-rich carbargillites at Buller Coalfield are interpreted as areas where aluminium was leached from adjacent high-moor bogs and precipitated in low lying drainage zones. During diagenesis and coalification, the more highly aluminous mineral matter has reacted with other mineral and chemical components to form chlorite, and with organically bound sodium to form dawsonite ($NaAlCO_3(OH)_2$).

In both Paparoa and Brunner coals, strontium occurs preferentially in crandallite, which is also a major host to barium. Strontium also occurs in calcium carbonate minerals, and may be organically bound. Sodium occurs to some extent as dawsonite (Brunner coals), or as smectite interlayers in illite (Paparoa coals), but is generally organically bound. Nickel occurs chiefly in organically bound form, but is also associated with illite-rich sediment in Brunner coals. In some Paparoa seams, post-depositional enrichment in nickel has occurred via roof and floor.

Mineral matter in West Coast subbituminous coals is dominated by organically bound calcium, and in one area, by sodium. At some localities, horizons of authigenic quartz are present.

The trends in mineral character generally support and extend peat accumulation models based on coal petrology, and thereby have relevance to coal exploration and coalfield development. The mineralogical data are applicable to aspects of coal characterisation, particularly the estimation of mineral matter/ash ratios and correction of volatile matter to mineral matter-free bases.

In general, the geochemical character of the coals presents few problems to conventional methods of coal utilisation. However, if the coals are washed, some potentially adverse elements may concentrate in ash, due to their intimate distribution in the coals.

CHAPTER 1

INTRODUCTION

1.1 SCOPE AND DEFINITIONS

This thesis documents a study of inorganic constituents of coals in the West Coast region, South Island, New Zealand. This area, comprising Westland and central and western parts of Nelson, contains New Zealand's only significant resources of bituminous coal, together with significant deposits of sub-bituminous coal.

The objectives of the study were to determine relative abundance, mode of occurrence, and origins of major and selected minor inorganic elements in West Coast coals, and to identify paleoenvironmental and other controls on these geochemical aspects. It is expected that these findings will have relevance to coal characterisation, coal exploration, coal utilization, and general geological interpretation of the West Coast coals and coal measures.

Several technical terms used in this dissertation are defined here to prevent misunderstanding of their meaning. The most important of these terms is mineral matter, which is used to describe all the inorganic components of coal, excluding free (uncombined) water. The remaining organic fraction, or "pure coal substance", is assumed to be restricted to the elements C, H, O, N, and S, occurring in organic combination. This definition conforms to common usage for bituminous coals (e.g., Gluskoter, 1975; Ward, 1977; Given and Yarzab, 1978; Gluskoter et al., 1981), and coal analytical standards (ISO 7404/1 pt.1, AS1038.22, AS2418.5). It is acknowledged that a proportion of the mineral matter, as defined, may occur in organic combination. The concept of mineral matter, as adopted for this report, is represented diagrammatically in Figure 1.1, taken from Gray (1983a). The fraction denoted by Gray as "pure coal mineral matter" is here termed organically bound mineral matter.

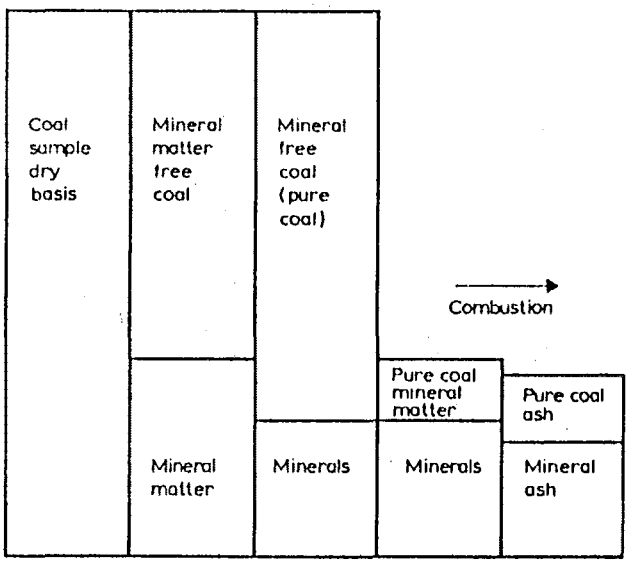


Figure 1 Illustration of terms used

Figure 1.1 Diagrammatic illustration of terminology for coal components, from Gray (1983a). In this thesis, the component defined by Gray as "pure coal mineral matter" is defined as "organically bound mineral matter", and no subdivision of ash is made.

In a scientific work dealing with mineral matter, the term ash should be used in a strict sense, i.e. the combustion residues of mineral matter. However, "high ash coal" and "low ash coal" are useful expressions implying high and low mineral matter content repectively, and these terms will be used in preference to the common equivalents "dirty coal" and "clean coal", which can be confused with dust content or burning characteristics. In current New Zealand terminology, a "high ash coal" yields more than 10% ash (air-dried basis; Bowen 1978).

Rank is defined as the degree of thermal maturity attained by a coal. Special problems encountered in assessing rank, as defined, for West Coast coals are discussed in detail by Newman and Newman (1982, 1983), Suggate and Lowery (1982), Suggate (1983), and Newman, J. (1985b). For the purposes of this thesis, a broad rank classification is satisfactory and the terminology of the ASTM system is used (Tables 1.5, 1.6).

Coal type is used in the strict sense, i.e. the maceral composition

of a coal. For West Coast bituminous coals, Newman (1985a) has shown important type distinctions on the basis of maceral subgroups as opposed to the principal maceral groups. Definition of coal petrographic terms can be found in Stach et al. (1982) or Ward (1984).

The term sediment, as used in this thesis, excludes organic material. This restricted definition is convenient when discussing swamp and basin history.

There is no universally accepted meaning for the term diagenesis. For simplicity, it is used in this work to describe all changes in mineral material from the time of deposition until coalification is complete. "Early diagenesis" means changes occurring from deposition to the end of biochemical coalification. This usage conforms to that of many coal petrologists, e.g., Teichmüller and Teichmüller (1982), Mackowsky (1982).

1.2 MINERAL MATTER IN COAL: A REVIEW

1.2.1 Introduction

It is appropriate to commence this dissertation with a review of developments in the science of mineral matter in coal. However, it is intended that this review should focus on those aspects which are chiefly applicable to the investigations detailed in this thesis. Published reviews and general discussions of mineral matter can be found in work by Mackowsky (1958, 1961, 1968, 1975, 1982), Watt (1968), Gluskoter (1975), Gluskoter et al. (1981), Ward (1977, 1986), Jenkins and Walker (1978), Fowkes (1978), Finkelman (1980), and Renton (1982). The references cited by these authors, particularly Watt (1968) and Ward (1986), provide a bibliography covering most of the important documented mineral matter work available. Additional citations covering North American publications to 1977 are listed, with abstracts, by Akers et al. (1978), and eastern European studies are quoted by Bouska (1981).

1.2.2 Development of mineral matter studies

It is not possible to identify a single, benchmark publication which introduced either the term mineral matter, with respect to coal, or the foundation of modern concepts concerning this subject. Numerous chemical analyses of coal ash were reported in 19th century literature, but little attempt was made to consider the mode of occurrence, or origin, of the ash constituents in the parent coals. During the early years of the 20th century, a more rigorous and scientific approach to determine the composition, distribution, genesis, and significance of mineral matter emerged in response to both the increasing consumption of coal, and the rapidly advancing technology of coal utilisation and beneficiation.

This emergence of modern concepts is demonstrated by North American literature, particularly by workers in the State of Illinois. Much of this early research was devoted to assessment of mineral matter/ash factors for correcting coal analyses (Parr, 1904; Parr and Wheeler, 1909; Brinsmaid, 1909; Parr, 1928, 1932; Theissen, 1934), although some petrographic studies were carried out (Selvig and Seaman, 1929; Ball, 1931; Cady and Leighton, 1933; Gauger et al. (1934).

Relevant British publications over this period focussed on comparing the abundance and composition of ash from different lithotypes (Stopes and Wheeler, 1918; Lessing, 1920, 1925; Baranov and Francis, 1922). In attempting to explain the observed differences in ash character, some of these authors (particularly Lessing) proposed or reviewed many important mineral matter controls which have subsequently been confirmed by modern research.

From the 1940's onward, mineral matter studies were more commonly based on direct mineralogical investigation, in comparison to most of the earlier work, which employed an indirect approach based on ash chemistry. Mineralogical investigations were enabled by the widespread application of instrumental techniques, chiefly X-ray diffraction, and improved methods of reflection microscopy. In Germany, M.Th.Mackowsky emerged as a leading authority on mineral matter, publishing extensively on this subject and setting up a widely recognised classification scheme (see 1.2.3).

Over the past 25 years, mineral matter studies have rapidly expanded, in response to advances in coal technology, especially coal conversion, and concern regarding environmental protection. Prominent examples of these studies are publications on coal characterisation (O'Gorman and Walker, 1971; Soong and Gluskoter, 1977; Walker et al., 1980; Gaigher, 1980), some of which involved paleoenvironmental considerations (Gluskoter, 1967; Rao and Gluskoter, 1973; Ward, 1977,1978). Much research was carried out on mineral matter and trace elements (e.g., Gluskoter et al., 1977; Kuhn et al., 1980; Finkelman, 1980), and on the development of specific techniques for investigating mineral matter (see 1.3).

1.2.3 Classification of mineral matter

Mineral matter has been variously classified according to one or more of the following criteria:

(i) Mineral group (e.g., silicates, carbonates, etc.)
(ii) Character of occurrence (e.g., in fractures, disseminated, etc.)
(iii) Time of mineral genesis
(iv) Process of mineral genesis

Mineragraphic subdivision is relatively straightforward and does not require any assumptions concerning mineral origin, although adequate mineralogical identification is needed. Most authors describing mineral matter provide a listing by mineral group, either alone or combined with some other classification scheme.

Character of occurrence provides a simple and basic method of mineral matter classification in the absence of mineralogical data. Most authors of early publications dealing with coal minerals or coal chemistry made a distinction between one fraction of mineral matter, which was finely disseminated and could not be physically removed, from another fraction which could be easily picked or washed out of the coal. These two divisions have been described by a number of different terms in the past (Table 1.1), but are now generally known as inherent and adventitious, respectively. The term "dirt" still appears in British coal literature, where it is chiefly applied to non-coal bands or beds, and

many North American authors retain usage of "intrinsic" and "extraneous".

Finely disseminated mineral matter which cannot be physically removed from coal	Coarse grains, nodules, infillings, etc, easily removed from coal	
true, fixed	heavier m.m., dirt	Bone (1918)
inherent	adventitious	Lessing (1920)
inherent	dirt	Lessing (1925)
inherent, intrinsic	dirt, extrinsic	Bone (1936)
inherent	extraneous	Edgecombe & Manning (1963)
disseminated	segregated	Yancy & Geer (1968)

Table 1.1 Various nomenclature applied to a basic, two-part classification of mineral matter in coal.

It is common for mineral matter to be classified according to either inferred time of formation, inferred process of formation, or both. Mackowsky (1961, 1968, 1975, 1982) presented a classification scheme primarily based on time of formation, with process of formation as a secondary division (Table 1.2). Mackowsky's inclusion of "transformation" in the epigenetic class alone may not be justified, for many such mineral alterations can occur diagenetically. A further anomaly of this scheme is the failure to acknowledge epigenetic kaolinite.

More recently, Ward (1986) outlined the nomenclature of mineral matter genesis (Table 1.3), using terms and definitions which more closely reflect current usage by English-speaking coal scientists. However, the definition of epigenetic may be an exception in this respect. Unless it can be shown that mineral deposition in fractures always postdates achievement of present (maximum) coal rank, Ward's definition must be regarded as too restricted. Mackowsky's classification scheme is widely used, but it is cumbersome and difficult to apply in practice. In particular, the syngenetic class is too broad to be useful. Gluskoter (1975) and Gluskoter et al., (1981) suggested as primary divisions, detrital (or allogenic) and authigenic, with a secondary subdivision of authigenic minerals into two classes: syngenetic (formed during initial stages of coalification) and epigenetic (formed subsequently).

Mineral Group	First stage of coalification		Second stage of coalification	
	Syngenetic formation synsedimentary-early diagenetic (intimately intergrown)		Epigenetic formation	
	Transported by water or wind	Newly formed	Deposited in fissures, cleats and cavities (coarsely intergrown)	Transformation of syngenetic minerals (intimately intergrown)
Clay Minerals	Kaolinite, Illite, Sericite, Clay Minerals with mixed-layer structure Montmorillonite, Tonstein			Illite, Chlorite
Carbonates		Siderite-Ankerite concretions, Dolomite, Calcite, Ankerite Siderite, Calcite	Ankerite Calcite Dolomite Ankerite in Fusite	
Sulphides		Pyrite concretions Melnikovite-Pyrite Coarse Pyrite (Marcasite) Concretions of FeS_2—$CuFeS_2$—ZnS Pyrite in Fusite	Pyrite Marcasite Zinc Sulphide (Sphalerite) Lead Sulphide (Galena) Copper Sulphide (Chalcopyrite)	Pyrite from the transformation of syngenetic concretions of $FeCO_3$
Oxides		Hematite	Goethite, Lepidocrocite ('Needle-Iron Ore')	
Quartz	Quartz grains	Chalcedony and Quartz from the weathering of Feldspar and Mica	Quartz	
Phosphates	Apatite	Phosphorite, Apatite		
Heavy minerals and accessory minerals	Zircon, Rutile, Tourmaline, Orthoclase, Biotite		Chlorides, Sulphates and Nitrates	

Table 1.2 Classification of minerals in coal by mineral genesis and mineralogical group. From Mackowsky (1982, Table12).

a) TIMES OF MINERAL FORMATION

SYNGENETIC — at the time the plant debris accumulated.
EARLY DIAGENETIC — shortly after burial by more peat or other sediment.
LATE DIAGENETIC — processes associated with deeper burial and rank advance.
EPIGENETIC — after the coal reached its present rank.

b) PROCESS OF MINERAL FORMATION

DETRITAL INPUT — solid particles washed or blown into peat swamp.
AUTHIGENESIS (or NEOFORMATION) — precipitated from solution or by biogenic processes.
DIAGENETIC ALTERATION — formed by interaction of other minerals with peat or swamp waters or by rank advance.

Table 1.3 Nomenclature for time and process of mineral matter genesis, from Ward (1986, Table 2).

It is noteworthy that the reproduction of Mackowsky's classification scheme by Gluskoter et al. (1981) suggests a major misinterpretation of the clay minerals section. Mackowsky clearly acknowledged that these minerals could be both detrital and authigenic in origin, yet Gluskoter et al. (1981, Table 7.5) allotted them a detrital class alone.

1.2.4 Sources of mineral matter in coal

Three sources of mineral matter can be defined as contributors to mineral matter in coal:

(i) Detrital, comprising material deposited by water or wind.

(ii) Vegetal, representing inorganic constituents, either solid or in solution, originally incorporated in the living plants which contribute to the peat debris.

(iii) Ground water, which can introduce dissolved inorganic matter from outside the peat body either before or after burial.

These sources have been recognised for many years, as demonstrated in summaries by Kendall (1916) and Lessing (1925). However, the relative importance of each source remains controversial. It is apparent that inorganic material from any source may be recycled via vegetation or ground water prior to fixation as mineral matter. Ground water is also recognised as the route for loss of inorganic matter from the swamp; such lost constituents may originate in either the vegetal or detrital material, as originally pointed out by Stopes and Wheeler (1918), and reiterated by Lessing (1925).

In the past, many coal scientists have equated inherent mineral matter with vegetal inorganic matter. This concept was supported by chemical studies of handpicked lithotypes (Lessing, 1920; Baranov and Francis, 1922; Lessing, 1925), and is probably still favoured by some authorities today. Both Mackowsky (1961) and Watt (1968) broadly accepted this theory, although Mackowsky acknowledged that "true inherent inorganic matter" (from plants) may be indistinguishable from "fixed adventitious inorganic matter", (intimately distributed mineral matter derived from ground water).

Apart from contributing dissolved inorganic matter, it is known that

plants deposit discrete, granular inorganic matter in peat swamps. Studies of recent peat have shown silica occurring as phytoliths (Finney and Farham 1968, Mackowsky 1975, 1982), and also as diatoms and sponge spicules (Renton and Cecil 1979, Andrejko et al. 1983, Davis et al. 1984). To date, there have been no positive identifications of these biogenic particles in coal, supporting the theory that biogenic silica would probably be destroyed by dissolution or reaction, before or during coalification (Bailey and Kosters, 1983; Upchurch et al. (1983); Davis et al., 1984).

1.2.5 Quartz

The biogenic contribution to silica in coal has been discussed above. Whereas the biogenic particles themselves may not survive in the peat or coal, this source can be expected to contribute dissolved silica which may be deposited as authigenic kaolinite or authigenic quartz.

Although most occurrences of quartz in coal can be recognised as detrital by using light or electron microscopy, authigenic quartz is known to occur as infillings in cleats, fractures, and fusinite cell structures, and in bands cementing clay (e.g., Kemezys and Taylor, 1964; Mackowsky, 1968), and more rarely, as idiomorphic crystals (Baker, 1946; Hoehne, 1949, 1953, 1954a, 1954b; Leskevich, 1959; Blattner, 1976; Soong and Blattner, 1986). Extensive silicification has been described from peat (e.g., Ting, 1972, 1977), and coal (e.g., Ward, 1978); quartz petrifaction of tree trunks and branches is well known, but appears to be more common in thin seams and carbonaceous horizons in coal measures than in thick coal.

The origin of fine grained quartz less than 10 μm in diameter is regarded as problematical (Botz and Hunt, 1986). Ward (1978) suggested that quartz appearing in the clay fraction of processed mineral matter might be authigenic.

Several sources for authigenic quartz have been proposed. Relict biogenic silica was suggested by Renton and Cecil (1979), although subsequent work (see above) indicates that this material will pass through a solution phase, and may be lost from the swamp or react to

form silicates. Other silica sources that have been proposed are decomposing or transforming silicates (Mackowsky, 1968; Renton, 1982), dissolution or recrystallisation of detrital quartz (Hoehne, 1953), or metasomatism caused by igneous intrusions (Kemezys and Taylor, 1964; Gluskoter et al., 1981).

1.2.6 Feldspar

Reports of minor amounts of feldspar in coal are common. Whereas some of these occurrences might represent contamination by non-coal lithologies, others (e.g., Ward, 1978) are reported from studies where sampling specifically excluded roof, floor and sediment bands.

In view of the known instability of feldspars in acidic leaching environments the occurrence of this mineral in coal is surprising. Furthermore, why feldspar should occur in some seams and not others, even within the same coal basin, has not been adequately explained. There has been no documentation of authigenic feldspar in coal, although such occurrences are known in sedimentary rocks. Ward (1978) suggested a possible pyroclastic origin for feldspar in some Australian seams, but otherwise, this mineral must be assumed to be detrital, and to have survived the combined effects of transport and deposition. Peat swamps which allowed feldspar to persist may have been less acid, and more stagnant or cation-rich than others where no feldspar survives. However, it appears that no corresponding evidence of environmental contrast has been found in maceral petrography or clay mineralogy. Similar evidence should also be found in situations where feldspar in coal is related to external influences, such as supply of fresh, unweathered sediment into the peat.

1.2.7 Clay minerals

In order to review the origin of clay minerals in coal it is first necessary to define the terms neoformation and transformation, which describe mineral origin. These terms were popularised by Millot (1970), but because his usage is confusing, the redefinition by Jeans (1971) is preferred, i.e.:

Neoformation: Crystallisation of a new mineral structure from simple and complex ions, in which there is no inheritance of a pre-existing mineral structure.
Transformation: Formation of a new mineral in which part or all of a pre-existing mineral structure is inherited.

The clay minerals group is generally regarded as the most abundant mineralogical class of mineral matter, and typically accounts for 30%-70% of mineral matter in coal. The clays are also considered important because of their significance to aspects of paleoenvironmental interpretation. Clay minerals found in coal are predominantly kaolinite, illite, and mixed layer illite-smectite, together with minor amounts of chlorite. Low temperature neoformation of quartz and clays (illite, smectite, and mixed layer) has been proposed by Renton and Cecil (1979), who even suggest that many partings and tonsteins in coal may represent zones of advanced degradation of organic matter. Although there is evidence that plant debris may contribute to the authigenic mineral matter, the contention of Renton and Cecil that "the majority of syngenetic minerals in coal originate within the swamp from amorphous silicates originally contained within the swamp plants" is not widely supported. Davis et al. (1984) point out that this theory is inconsistent with the maceral petrography of the coals cited as examples by Renton and Cecil. Furthermore, studies of modern swamps by Davis et al., and Bailey and Kosters (1983) both lead to the conclusion that quartz and clays in peat are predominantly detrital in origin.

However, many authors have argued in support of neoformational and transformational origins for clay minerals in coal. Neoformation of kaolinite in peat and coal is commonly demonstrated by the occurrence of this mineral infilling maceral pore structures and fractures. There is ample experimental evidence to show how such kaolinite might develop through interaction of solutions or gels of silica and alumina, (e.g., Kittrick, 1970; Linares and Huertas, 1971; La Iglesia-Fernandez and Martin-Vivaldi, 1972).

The recognition of authigenic kaolinite has led to problems in estimating what proportion of -2 μm (clay fraction) kaolinite has this origin, and what proportion is detrital and might truly indicate the depositional

environment. Gluskoter (1967), working on the Illinois No. 6 coal, believed that the distribution of -2 μm kaolinite, albeit partly authigenic, was consistent with the depositional pattern of the coal basin. However, in a later study based on the underlying No.5 coal, Ward (1977) considered the low abundance of -2 μm kaolinite in channel areas to indicate a poor relationship with the expected sedimentation pattern, even though the overall kaolinite/illite and kaolinite/mixed layer relationships were the same as those found by Gluskoter. The uncertainty regarding the origin of -2μm kaolinite in coal, and the significance of this fraction, remains unsolved. Particular points which remain to be addressed are:

(i) The degree to which preparation methods influence the relative proportions of different -2 μm clays.

(ii) The extent to which chemical remobilisation and redistribution of clays occur during peat accumulation, and how this affects their relative proportions in the clay fraction.

(iii) The extent to which remobilisation and redistribution of clays occur during and after coalification.

Ward (1977, 1978) briefly acknowledges the possibility of (iii), above, but the other factors appear to have been ignored. Kaolinite in cleats and fractures is good evidence for syn- or post-coalification mobility, which is further demonstrated by the work of Botz and Hart (1983), wherein tectonically disturbed areas of coal seams were shown to be depleted in kaolinite. Effect (ii), above, may be even more significant, yet may take place without leaving obvious evidence. Widespread remobilisation, or at least in situ recrystallisation, of kaolinite would explain the high degree of crystallinity commonly observed for this mineral in coal.

Neither simple recrystallisation, nor local remobilisation of original sedimentary kaolinite within peat or coal can be expected to alter the gross pattern of kaolinite sedimentation within a coal basin, unless significant transport to or from adjacent non-coal lithologies takes place. It can be argued that if recrystallisation and local remobilisation predominate over introduction of neoformed kaolinite from external or distant sources, interpretations based on clay mineral abundances should use total kaolinite, rather than -2 μm kaolinite, as a variable. Gaigher (1980) preferred to analyse whole low-temperature ash for clay minerals,

on the grounds that it may be more meaningful than a clay fraction.

The foregoing discussion applies chiefly to kaolinite, but may also be valid for other clays occurring in coal. As described above, the possible occurrence of neoformed illite, smectite, and mixed layer clays within the swamp has been proposed by Renton and Cecil (1979). Mackowsky (1968, 1975, 1982) admits the possibility that some of these minerals might be neoformed as well as detrital. Many authors invoke transformation to explain the observed pattern of clay minerals in coal seams and coal measure sediments. Ionic regrading of leached, degraded clay silicates entering a marine environment is well documented (e.g., Weaver, 1967; Curtis and Spears, 1971; Weaver and Pollard, 1973), but transformations in acidic, nonmarine environments are not so well understood. Experimental evidence has demonstrated a progression of transformations which occur in acid conditions, e.g., the conversion of micas to smectites (Millot, 1970), and ultimately the destruction of smectite to leave kaolinite (Poncelet and Brindley, 1976; Staub and Cohen, 1978). It is apparent that silicate degradation-regradation reactions and the stability of the mineral phases involved is controlled by pH and concentration of different ionic species, particularly K^+ and other metal cations.

Gluskoter (1967) suggested that some illite and chlorite in Illinois coals could be explained by the regrading of mixed layer clays, in response to transport into a higher salinity region of the depositional basin. In contrast, Ward (1977) proposed that the illite component of some Illinois coals was residual in character, citing experiments by Huang and Keller (1972a), who sharpened the illite 10Å x-ray diffraction peak by protracted treatment of the clay with an organic acid, apparently preferentially dissolving the disordered and expandable fractions. This theory seems to have been subsequently ignored in the literature. Later work by Ward (1978) contains the proposal that at least some of the illite-smectite mixed layer clays were precipitated from solution; presumably some combination of both dissolution and precipitation could occur within a peat swamp if adequate geochemical gradients exist.

There is some confusion concerning the origin of the small amounts of chlorite occasionally found in coal. Mackowsky (1968, 1975, 1982) lists both chlorite and illite as neoformed minerals appearing in the "second

stage of coalification" (deep burial), but the formation conditions for these minerals are not discussed, apart from a brief reference (1968) which shows that anthracitic rank was envisaged. Ward (1977) suggested a (?syndepositional) neoformation origin for chlorite in Illinois coals, but later (1978), considered a chlorite occurrence in an Australian coal to be detrital. In a further publication, Ward (1986) reassessed the Australian chlorite as being of metamorphic-transformation origin, pointing out that the coal, from Baralaba in Queensland, is of semianthracitic rank. In adopting this stance, Ward also revised his views on chlorite in the lower rank, bituminous coals of Illinois, which contain traces of chlorite at a few localities; these occurrences he now considered possibly detrital, despite the general view that chlorite is readily destroyed in the acidic conditions expected in peat swamps. It is surprising, however, that low temperature synthesis during early coalification has not been considered by the authors who encounter chlorite in coals.

One useful approach to estimating the net change in clay mineralogy when sediment enters peat swamps is to compare mineral matter in peat or coal with ajacent non-coal strata, usually roof and floor rocks. This approach has been used in studies by Gluskoter (1967), and Ward (1977, 1978). Mineral matter in coal commonly contains more kaolinite, less quartz and illite, and little or no chlorite and feldspar in comparison to non-coal lithologies. Although Ward emphasised the need to compare only muddy lithologies near the coal to the minerals in the seam itself, there remains some uncertainty as to whether non-coal lithologies adequately represent sedimentary supply to the swamp during peat accumulation. Differences can arise from variation in source or character of transport and deposition. Furthermore, postdepositional changes can affect roof, floor, and partings lithologies as a result of in situ weathering, or alteration by swamp ground water (Staub and Cohen, 1978).

While it can be acknowledged that the principal controls on quartz and clay mineral matter are, as discussed above, paleoenvironmental factors in the zone of deposition, and early post-depositional diagenesis, the effects of middle and late diagenesis may also be significant. However, apart from epigenetic mineral formation, these effects are largely unknown. Mackowsky's reference to high temperature formation of illite and chlorite has been mentioned above. Progressive thermal alteration

of smectite and mixed layer clays to illite, together with a general increase in the crystallinity of illite, can be recognised from approximately mid-high volatile bituminous rank in non-coal sediments (e.g., Kisch, 1969; Pevear et al., 1980), although it is not clear how closely coal minerals follow this change.

Gaigher (1980) described a special case of mineral matter development in some South African coals, in which igneous intrusions promoted the growth of illite, and possibly chlorite, at the expense of kaolinite. Local heating and K-metasomatism appeared to have occurred in the seams at the brown coal stage, while the coal retained a high permeability. In coals subject to normal geothermal maturation, loss of permeability is probably the major factor limiting postburial alteration of mineral matter, if the analogy of non-coal sedimentary sequences (Milne and Early, 1958) can be applied.

1.2.8 Carbonates

Carbonate minerals found in coal are principally siderite, calcite, and dolomite. Siderite occurs as nodules and lenticular masses, ranging from microscopic size to more than a metre in length. Compaction textures surrounding the nodules, and uncompressed plant remains within the nodules, show that siderite was formed in the early stages of coalification (e.g., Kemezys and Taylor, 1964), but on theoretical grounds, it is unlikely to have formed in the uppermost, acidic peat surface (Curtis and Spears, 1968). Siderite is also found in epigenetic form, infilling fractures and cleats. Calcite and dolomite also occur in early diagenetic, concretionary form ("coal balls"), but are more common as fracture fillings. Some dolomite in coal is of the ferroan variety, ankerite (Mackowsky, 1968).

Oxygen isotope studies have provided useful information on the formation conditions for carbonate mineral matter. Gould and Smith (1979) used isotopic evidence to show that nodular siderite formed beneath the zone of surface oxidation, by reaction between ferrous iron and dissolved CO_2 produced by early anaerobic fermentation of organic matter. More recently, Botz et al., (1986) used isotopic data to derive a formation temperature of 20°C for nodular siderite in an Australian bituminous

coal. In contrast, formation temperatures in the range 34°–70° were obtained for epigenetic carbonates.

The presence of nodular siderite in coal or coal measures is interpreted as indicating the absence of marine influence during, or soon after, peat accumulation. This reasoning is based on the assumption that even slightly brackish water contains enough reduceable sulphate to react with available iron in peat to form sulphides. Conversely, the presence of nodular calcite or dolomite in coal or coal measures is considered to indicate the influence of marine water during deposition (Mackowsky, 1968, 1975, 1982; Matsumoto and Iijima, 1981; Teichmüller and Teichmüller, 1982), which would both reduce acidity and supply the necessary cations. However, carbonates also form in neutral to alkaline environments of peat accumulation which are not necessarily marine influenced, but owe their high pH and high calcium content to adjacent or underlying limestone bedrock (Teichmüller and Teichmüller, 1982).

Aragonite has been reported in Indian bituminous coals (Mitra, 1954), and also in North American lignite (O'Gorman and Walker, 1971) where it is accompanied by calcium sulphate, and may be of recent origin related to surface weathering.

The unusual mineral dawsonite ($NaAlCO_3[OH_2]$) is listed with carbonates by Ward, because of an epigenetic occurrence in coal in the Sydney Basin (Loughnan and Goldberry, 1972). The origin and significance of this mineral in coal is discussed later in this thesis.

1.2.9 Sulphides

Sulphide minerals in coal essentially comprise pyrite, which is ubiquitous, and marcasite, which is less common. Rarely, minor amounts of ore minerals such as sphalerite and galena are found, usually in veinlets.

A concise, comprehensive review of sulphur in coal, including sulphide and sulphate minerals, can be found in a recent publication by Frankie and Hower (1987). Despite a great deal of research into coal sulphide morphology, composition, and petrographic association, many

aspects of sulphide origin remain uncertain or poorly substantiated. Coal sulphides are entirely authigenic, and apart from some transformational and epigenetic forms, can be considered to be the result of interaction between soluble iron and ionic sulphide species created by bacterial reduction of sulphate, at or beneath the peat surface. This concept is largely drawn from studies of marine sediment (e.g., Berner, 1970), and supported by observations from modern peat (Casagrande et al., 1977; Altschuler et al., 1983). Thus, marine or brackish water entering a peat swamp is believed to be the cause of fine-grained pyrite deposition in the form of framboids, fine concretions, and microscopic crystals (King and Renton, 1979; Donaldson et al., 1980).

However, substantial growth of sulphide in compressed peat, and possibly low rank coal, is thought to occur in response to circulation of sulphur-bearing ground water. This origin, first suggested by White and Theissen (1913), is now widely accepted, and is believed to result in overgrowths on pre-existing crystals and framboids, and deposition of massive aggregates (Donaldson et al.). The timing of sulphide infilling and replacement of tissue structure is uncertain.

Post-burial sulphide growth also occurs by replacement of siderite, as illustrated by Mackowsky (1968), and confirmed experimentally by Smythe (1966).

It is unclear as to whether post-burial sulphide enrichment involves simple permeation of sediment by seawater, or whether sulphur can be remobilised from overlying or underlying marine sediment. Similarly, there is no clear evidence to show whether such sulphide enrichment involves transport of both iron and sulphur, or one component alone. Sulphide replacement of siderite presumably involves influx of sulphur alone, either as reduceable sulphate or sulphide. Conversely, it has been proposed that epigenetic sulphide in cleats and fractures results from a reaction between iron-bearing solutions and sulphide already present in the coal (Neavel, 1966).

1.2.10 Minor mineral groups

Apart from the minerals so far discussed, coal commonly contains a number of other mineral species, which usually constitute a very minor part of the total mineral matter. For convenience, these minor minerals can be grouped under the following headings:

(i) Oxides and hydroxides
(ii) Phosphates
(iii) Sulphates
(iv) Trace minerals

Oxides and hydroxides. If quartz is excluded, this group essentially comprises Al, Ti, and Fe species. Diaspore in coal is reported by a number of authors, e.g., Mackowsky (1975, 1982), but no details of occurrence are given. Boehmite is listed without further description by both Bouska (1981) and Adolphi and Storr (1985).

The TiO_2 minerals rutile, brookite, and anatase have been widely reported as minor minerals in coal; of these three minerals, rutile and anatase appear to be the most commonly encountered. Rutile in coal is considered entirely detrital by Mackowsky (1968, 1975, 1982), but all three minerals could result from low temperature authigenic processes (Deer et al., 1962).

Magnetite, hematite, goethite, lepidocrocite, and limonite have all been reported as occurring in coal, but little consideration has been given to their origin. Mackowsky's classification tables show hematite as neoformed during early coalification, and both goethite and lepidocrocite as epigenetic (Table 1.2).

For the latter two minerals, their classification is consistent with an origin attributable to post-uplift weathering, but the concept of synsedimentary or early diagenetic hematite (or precursor) in coal is difficult to accept. The highly reducing environment existing beneath the surface of a peat swamp cannot be expected to favour iron oxide or iron hydroxide deposition (e.g., Curtis and Spears, 1968; Curtis and Coleman, 1986). Although an emergent, well aerated peat surface might undergo intermittent oxidation, any iron oxide/hydroxide formed at that stage

would have to survive dissolution, carbonation, and possibly sulphidation reactions during later burial.

A possible exception to the above argument is bog iron ore, referred to by Mackowsky (1975, 1982), which can precipitate in oxidising enviroments at the margins of peat swamps (Blatt, et al., 1972). Such environments are not, however, characteristic of zones of significant peat accumulation.

Phosphates. The most widely reported phosphate mineral in coal is apatite. Although normally too sparse to appear on x-ray diffractograms of mineral matter, apatite has been identified by optical microscopy, and has been shown to be present in coals on the basis of fluorine liberation temperatures (Crossley, 1944), or a consistent P/F relationship (Durie and Schafer, 1964). A consistent P/Ca relationship has also been used to infer the presence of apatite (Shiboaka, 1971), although this could also indicate crandallite. Mackowsky (1975, 1982) illustrated colliform phosphorite of unknown mineralogy, and idiomorphic apatite, both of authigenic origin. However, Mackowsky also acknowledged a detrital origin for apatite. Ward (1978) considered apatite in Australian coals to be detrital.

Complex aluminophosphate minerals of the crandallite group (see 3.10) also occur in coal. The variety goyazite has been described from some Australian coals (Ward, 1974, 1978), and gorceixite, goyazite, and crandallite from various coals of U.S.A. (Finkelman et al., 1979; Finkelman, 1980). Ward (1978) implies an early diagenetic origin for the Australian goyazite, but some of the American crandallites which occur with sphalerite (Finkelman et al.) may be of later origin.

Sulphates. With the possible exception of barite, it is probable that all sulphate minerals reported from coal can be attributed to deposition of post-uplift weathering products by ground water, direct oxidation of exposed or stored coal, or synthesis during ashing procedures. This point remains obscure. Renton (1982) considered that "an unresolved question exists as to whether these (sulphate) minerals represent original coal minerals", and Ward (1986) stated "some sulphate minerals may occur in their own right as inherent mineral components of essentially

unaltered coals". However, this has not so far been demonstrated by example. Deposition of synsedimentary or diagenetic sulphate appears unlikely, on theoretical grounds; not only are these minerals (except barite) highly soluble, but sulphate is unlikely to persist in the organic matter environment. Curtis and Coleman (1986) point out that "if sulphate is available, it will be reduced wherever and whenever sufficient organic matter is present to eliminate molecular oxygen and act as a substrate for microbes".

Epigenetic sulphates, principally of iron and calcium, are common at shallow depths in many coal-bearing areas. Well developed gypsum veinlets several centimetres in thickness in Australian coal seams have been attributed to the present arid climate in the coalfield region (Kemezys and Taylor, 1964), allowing dissolved minerals to accumulate from evaporating ground water.

Many different iron sulphate minerals have been reported from coal, particularly by users of Mössbauer spectroscopy (e.g., Montano, 1977; Huggins and Huffman, 1979), which is the most satisfactory method of identifying these minerals. Sulphate formation by oxidation of sulphide is often noted in stored coal samples (e.g., Ward, 1977). Similar reactions can take place during low-temperature ashing, when SO_3 and H_2SO_4 are formed and react with carbonate minerals (Given et al., 1975). When low rank (subbituminous and lignite) coals containing organic calcium are low-temperature ashed, all or most of this calcium is converted to sulphate if sufficient organic sulphur is present in the coal (Given and Yarzab, 1978; Miller et. al., 1979; Adolphi and Storr, 1985). In scientific terms, the recognition and recording of sulphates in coal is chiefly useful for demonstrating that some other, pre-existing mineral phase may have been destroyed.

Barite is widely reported in coals of all ranks (Finkelman, 1980), but the origin of this mineral is uncertain. Where seen, it occurs epigenetically in fractures.

Trace minerals. Lists of minerals reported from coal (e.g., Gluskoter et al., 1981) include a large number of mineral species which occur in trace amounts, often detectable as single or sporadic grains by optical

microscopy or SEM microanalyser. Some of these minerals are reported from carbominerites, tonsteins, or partings, and may not occur in coal proper.

A number of chemically resistant heavy minerals, such as zircon, tourmaline and garnet, are well documented as trace minerals in coal, and can be expected to result from detrital sedimentation, or possibly ashfalls. However, the status of poorly resistant minerals such as augite and hornblende as coal minerals must be viewed as potentially suspect, particularly where identifications have been made on the basis of SEM microanalysis alone. Furthermore, possible contamination by admixed roof, floor, or other lithologies must be considered when trace mineral identifications are made.

A number of minor sulphides and carbonates occur in coals, usually in epigenetic form, accompanying a major mineral such as pyrite or calcite.

1.2.11 "Organically bound" mineral matter.

The broad definition of mineral matter includes inorganic matter chemically bound to the organic coal substance or dissolved in pore water. This inorganic material is generally of minor importance at bituminous and higher ranks, but commonly accounts for the bulk of total inorganic matter in subbituminous coals and lignite. This class of mineral matter essentially comprises leachable salts, and entirely or substantially exchangeable cations, of Ca, Mg, Na, K, Fe and Al.

Acknowledging the importance of organically bound mineral matter in low rank coals, Kiss and King (1977, 1979) divided the inorganic matter in lignite into two groups, defined as "minerals" (particulate, + Al_2O_3) and "organics" (Na + Mg + Ca + Fe + NaCl). A similar approach has been used by Gray (1983a), who defined "minerals" and "pure coal mineral matter", respectively (Figure 1.1). These terms may be too confusing for general use.

The peat-forming process commences with humification, whereby lignin and cellulose are converted to humic acids. This process occurs

rapidly near the peat surface, where biochemical oxidation takes place, and more slowly as an anaerobic process at depth during the peat compression and brown coal stages. During burial, humic acids lose their hydroxyl and carboxyl groups and form gelified humins, the precursors of vitrinite. While the humic acid carboxyl groups exist, various cations may be bound to these sites to form humates (Teichmüller, 1982).

As coalification proceeds, metallic cations liberated from the decomposing humates are progressively concentrated in pore water, and pH rises (Renton, 1982). When bituminous rank is attained, elimination of carboxylate groups is virtually complete, although these species are known to persist in some high volatile bituminous C coals (Given and Yarzab, 1978).

The humification sequence described above is supported by studies of modern peats and brown coal. However, subsequent reactions involving loss of carboxylates are poorly understood. Some authors, e.g., Renton (1982) and Adolphi and Storr (1985), assume that cationic elements released from humates during early coalification proceed to react with anions to produce crystalline minerals such as calcite, dolomite, siderite, and pyrite. While no specific evidence can be shown to dispute this general hypothesis, it is probable that other processes contribute to the post-burial formation of these minerals.

The source of cations bonded to humates has been attributed to swamp vegetation (e.g., the "true inherent inorganic matter" described by Mackowsky, 1961), although most authors acknowledge the potential input of dissolved inorganic matter in ground water. Miller and Given (1986) emphasize the rapid and reversable nature of the cation exchange processes in peat and lignite, pointing out that the cationic composition should be in equilibrium with surrounding surface or ground water.

A major loss of vegetal inorganic matter takes place at the onset of peatification, near the swamp surface; Renton (1982) considers that by simple calculation, more than 90% of original plant inorganic material must be removed to produce a typical, low ash bituminous coal. Gross differences in inorganic matter composition between lignite, subbituminous coal, and bituminous coal are also explained by loss of inorgani-

cally bound elements to ground water at a later stage, during coalification (e.g., Fowkes, 1978).

A small fraction of the organically bound mineral matter consists of metals held in the coal substance by organometallic complexes unrelated to carboxyl groups. This fraction, which tends to be non-exchangeable and not eliminated from the coal during maturation, is largely restricted to certain trace elements (e.g., Zubovic et al., 1960, 1961).

Assignment of elements in coal to the inorganically bound group is commonly done either by cation exchange studies, or by analysing a series of float-sink fractions (e.g., Gluskoter et al., 1977). However, as pointed out by Finkelman (1980), "organic affinity" determined by gravity separations could simply reflect a uniform, intimate distribution of finely particulate minerals. For this reason, elements displaying preferential concentration in organic-rich fractions of coal are better classed as organically associated unless independent evidence of organic bonding can be demonstrated.

1.3 SEPARATION AND ANALYSIS OF MINERAL MATTER

1.3.1 Separation of mineral matter from coal

Mineral matter in coal can be investigated by a large number of different laboratory techniques, which can be classified into two groups as follows:

(i) Analysis of whole coal.

(ii) Analysis of mineral matter, concentrated or separated from the parent coal so as to eliminate most or all of the organic matrix.

Analysis of mineral matter in whole coal samples ensures that no changes affect the mineral components during sample preparation, but the organic coal substance will dilute the inorganic fraction, and may impose interference on the analytical results.

Methods of concentrating or isolating mineral matter are shown in Figure 1.2. Chemical leaching methods are used for special purposes,

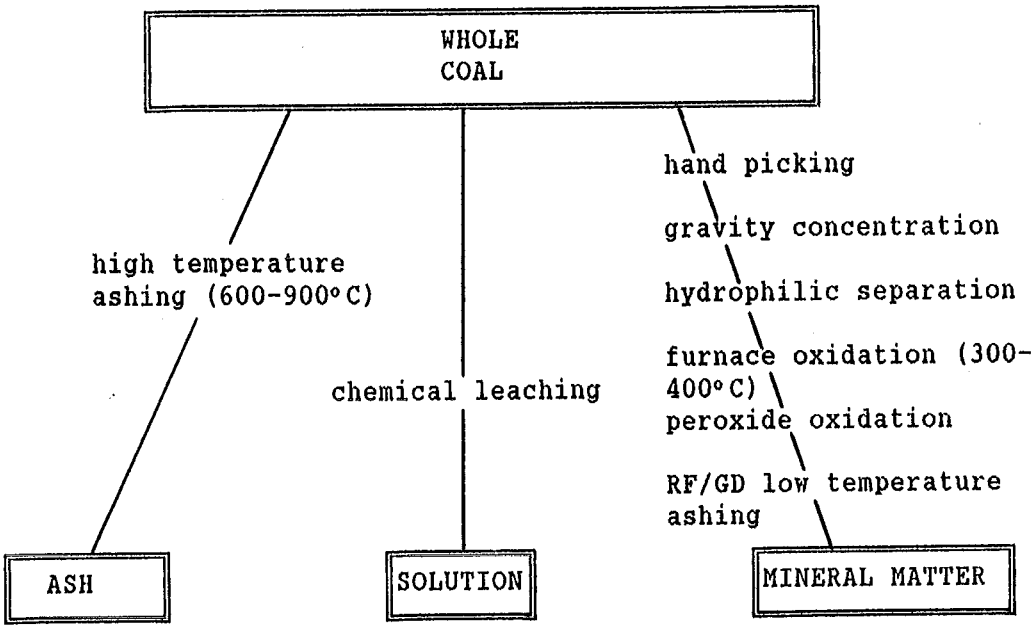


Figure 1.2 Laboratory methods of separating mineral matter from coal.

such as determination of exchangeable cations, total carbonate, or total sulphide. Rarely, acid leaching methods are used to determine total mineral matter. High temperature ashing is a standard technique for isolating the inorganic fraction of coal for elemental analysis; the resulting ash is of little value for direct mineralogical investigation, due to the severe alteration to most mineral species other than quartz and micas.

Several methods for nondestructively separating mineral matter from coal have evolved. Hand picking was the earliest of such methods, and is still used for special purposes such as isotope analysis, but is limited to coarse mineral grains, bands, or veins. Hydrophilic separation (Millot, 1958) and gravity concentration does not yield an organic-free mineral fraction, and may not recover finely dispersed mineral matter.

All of the low-temperature oxidation techniques (Figure 1.2) are capable of producing an organic-free residue, but certain changes to the mineralogy may occur. The dry methods may oxidise sulphides, decompose carbonates, and synthesise new compounds. The furnace oxidation method involves the highest temperatures, and is most damag-

ing to sulphides, clays, and other heat-sensitive minerals. Wet oxidation using hydrogen peroxide has been successfully used by Ward (1974), but destroys carbonate minerals and may form synthetic compounds. Radio frequency (RF) plasma oxidation has become a conventional method for the preparation of mineral matter samples, to the extent that "low temperature ash" is now synonymous with RF plasma oxidation residues.

The advantages, limitations, and operating conditions for RF plasma oxidation have discussed by Frazer and Belcher (1973), Jenkins and Walker (1978), and Miller et al., (1979). More recently, it has been shown that a plasma excited by glow discharge (GD) from high voltage electrodes produces better results (Adolphi and Storr, 1985).

1.3.2 Methods for analysis and investigation of mineral matter

The many methods which have been employed in mineral matter investigations will not be detailed here, but the most important techniques are summarised in Table 1.4. Descriptions of the various instrumental methods, as applied to mineral matter, can be found in publications by Watt (1968), Ruch et al., (1974), Jenkins and Walker (1978), Gluskoter et al., (1981), and Ward (1986). Several chapters in Karr (1979) are devoted to specific techniques.

METHOD		APPLICATION		
		Whole coal	Mineral matter	Ash
Light microscopy		*	+	
Scanning electron microscope/ probe microanalyser	(SEM)	+	+	+
X-ray diffraction	(XRD)	+	*	
X-ray fluorescence	(XRF)	*	+	*
Neutron activation analysis	(NAA)	+	+	+
Differential thermal analysis	(DTA)	+	+	
Infra-red spectroscopy:				
transmission dispersive	(IR)	+	+	
transmission Fourier tr.	(FTIR)		*	
reflected Fourier trans.	(FTIR)	+	+	
Mössbauer spectroscopy		+	+	
Nuclear magnetic resonance	(NMR)	+	+	

Table 1.4 Analytical methods for mineral matter in coal
Applicability: * major + minor

X-ray diffraction has remained the most widely used method of mineral matter analysis since RF oxidation was introduced. However, optical microscopy continues to be important, because it provides a simple method of mineral identification in tandem with maceral petrography, and also provides valuable information on the physical characteristics of minerals, their interrelationships, and their maceral associations. Fourier transform infrared analysis (FTIR) demonstrates considerable potential for mineral matter analysis (Painter et al., 1978), although the technique is not yet in common use.

X-ray fluorescence and neutron activation do not yield direct mineralogical data, but are valuable methods for determining bulk elemental composition, and are ideally used in conjunction with another technique which identifies mineral species.

Omitted from Table 1.4 and this discussion are the wet chemical methods, which are used for both specific mineralogical determinations (1.3.1), or chemical analyses.

1.4 COAL DEPOSITS OF THE "WEST COAST"

The "West Coast" coalfields of New Zealand are traditionally recognised as those located in the Westland - Western Nelson region (Figure 1.3). The geological history of these coalfields has, in many cases, been strongly influenced by tectonic activity, both during and after the periods of coal measure accumulation. This activity has resulted in coals which vary widely in type, rank, geochemical character, and geological setting (Tables 1.5 & 1.6). General stratigraphic relationships between deposits are shown in Figure 1.4.

The following outline of coal measure history and distribution is drawn from comprehensive descriptions of the coal measures and associated coals in publications by Gage (1952), Nathan (1974, 1976), Bowman and Newman (1983), and in J. Newman's (1985a, 1987) detailed paleoenvironmental and coal type studies.

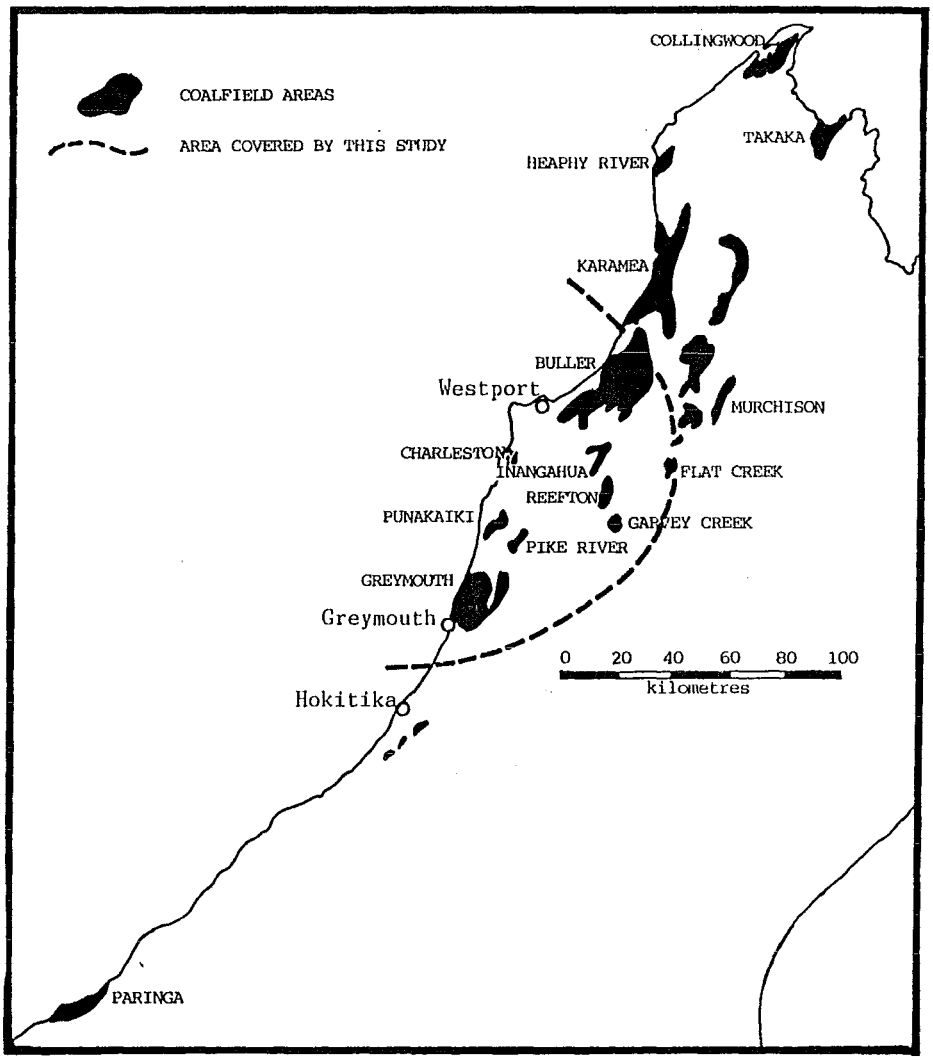


Figure 1.3 Location of coalfields in the West Coast region, with delineation of the area encompassed by the present study.

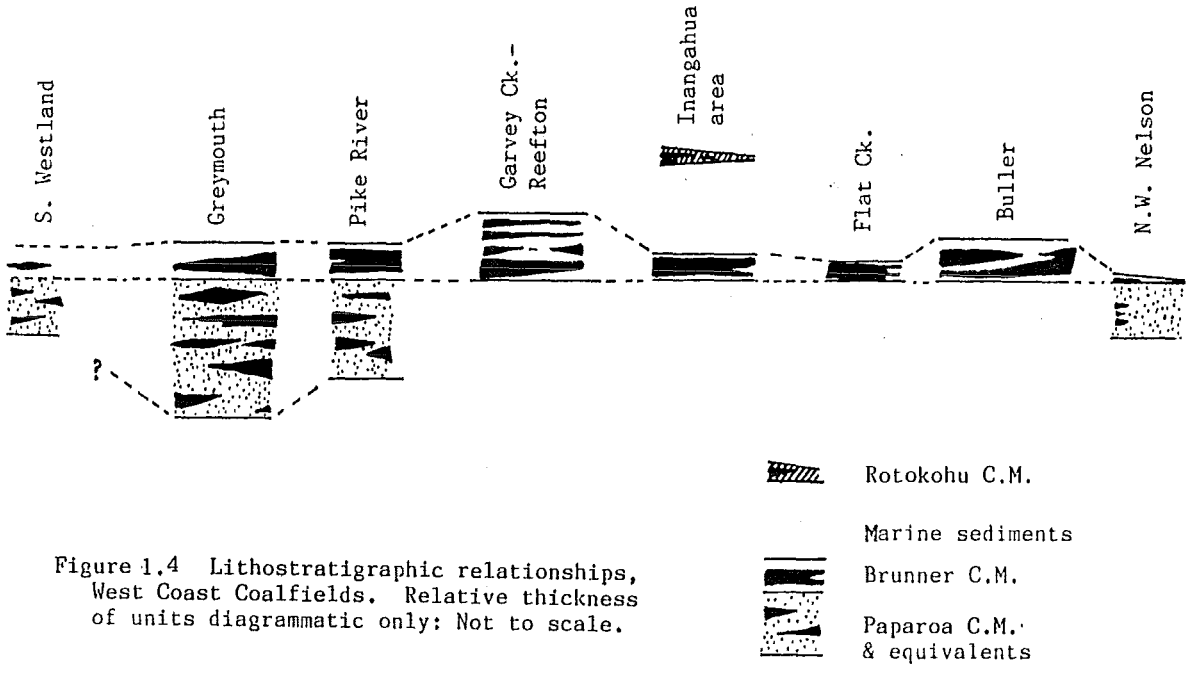


Figure 1.4 Lithostratigraphic relationships, West Coast Coalfields. Relative thickness of units diagrammatic only: Not to scale.

Table 1.5 Details of West Coast coal deposits included in this study.

COALFIELD	ESTIMATED RECOVERABLE RESERVES (m. tonnes)	RANK (ASTM)	COAL MEASURE HORIZON	SAMPLING, THIS STUDY
Buller	51.5*	lvb-hvAb	Brunner	drillholes, mine workings
Inangahua	6.7	subC-hvAb	Brunner + Rotokohu	run-of-mine, workings, outcrop
Flat Creek (Murchison)	1.0	?-hvAb-?	Brunner	old opencast
Reefton	6.3	hvAb-hvCb	Brunner	run-of-mine
Garvey Creek	6.1	hvAb-hvBb	Brunner	drillholes
Charleston	11.7	subA-subC	Brunner	opencast mine, run-of-mine
Pike River	15.0*	hvAb	Brunner+ Paparoa	drillholes, outcrop
Greymouth	77.3*	lvb-hvCb	Brunner+ Paparoa	drillholes, mine workings, outcrop

*May be substantially increased as a result of recent drilling

Reserve data from Taylor & Kunz (1983) and other sources.
Recoverability is assumed to be 50% of coal-in-ground (underground mining, to 400m depth).

1.4.1 Introduction

The oldest mineable coal-bearing units in the West Coast region are the Paparoa Coal Measures, a thick sequence of freshwater stream and lake sediments of late Cretaceous and early Tertiary age (Haumurian-Teurian), which accumulated in elongate, rift-controlled intermontane basins aligned approximately parallel to the present western coastline. These deposits were once extensive, and probably contained very large amounts of high quality coal, but subsequent uplift and erosion has reduced them to relatively small remnants, chiefly at Greymouth and Pike River.

Peat formation occurred intermittently throughout accumulation of the Paparoa Coal Measures, resulting in seam development at many different horizons. At Greymouth, four coal-bearing units are broadly delineated by intervening lake deposits, reflecting an overall history of cyclic variation between fluvial and lacustrine environments.

The onset of regional subsidence in early Tertiary time resulted in deposition of the Brunner Coal Measures, characterised by widespread

Abbreviation	Class	Group	Fixed carbon limits (%) (dry, mineral-matter-free basis) ≥	Fixed carbon limits (%) (dry, mineral-matter-free basis) <	Volatile matter limits (%) (dry, mineral-matter-free basis) >	Volatile matter limits (%) (dry, mineral-matter-free basis) ≥	Calorific value limits (Btu/lb) (moist mineral-matter-free basis) ≥	Calorific value limits (Btu/lb) (moist mineral-matter-free basis) <	Agglomerating character
	I. Anthracitic								
		1. Meta-anthracite	98	—	—	2	—	—	nonagglomerating
		2. Anthracite	92	98	2	8	—	—	
		3. Semianthracite	86	92	8	14	—	—	
	II. Bituminous								
lvb		1. Low volatile bituminous coal	78	86	14	22	—	—	commonly agglomerating
mvb		2. Medium volatile bituminous coal	69	78	22	31	—	—	
hvAb		3. High volatile A bituminous coal	—	69	31	—	14,000	—	
hvBb		4. High volatile B bituminous coal	—	—	—	—	13,000	14,000	
hvCb		5. High volatile C bituminous coal	—	—	—	—	11,500	13,000	
							10,500	11,500	agglomerating
	III. Subbituminous								
SubA		1. Subbituminous A coal	—	—	—	—	10,500	11,500	nonagglomerating
SubB		2. Subbituminous B coal	—	—	—	—	9,500	10,500	
SubC		3. Subbituminous C coal	—	—	—	—	8,300	9,500	
	IV. Lignitic								
		1. Lignite A	—	—	—	—	6,300	8,300	
		2. Lignite B	—	—	—	—	—	6,300	

Table 1.6 ASTM classification of coals by rank (adapted from Montgomery, 1978).

establishment of peat-forming environments, mainly in paralic (marginal marine) areas on an eroded land mass of low relief. Although most Brunner deposits are of Eocene age, Brunner Coal Measure sedimentation extends from Paleocene to Oligocene time in different areas, depending on paleogeographic circumstances (Suggate, 1950; Nathan et al., 1986). In comparison to the Paparoa Coal Measures, Brunner Coal Measures typically comprise a relatively thin sequence, frequently quartzose, resting unconformably on an eroded and weathered surface. The coal usually occurs as a single seam, and commonly shows a distinct petrographic character attributed to slow peat accumulation, advanced biochemical degradation, and possibly a cellulose-rich swamp flora (Newman, 1985a; Newman & Newman, 1982).

Brunner peat accumulation was terminated by marine transgression, and followed by burial beneath marine sediments. The marine incursion has resulted in typically high sulpur contents for Brunner coal, the sulphur being derived either directly from seawater, or indirectly via marine sediments, or by some combination of both sources (Suggate, 1959).

Small deposits of Brunner coal occur very widely in the West Coast region, often in marginal or uneconomic quantities, but major deposits are located at Buller, Reefton, Pike River, and Greymouth.

Coal measures equivalent in age to the Paparoa Coal Measures occur in North West Nelson (Pakawau Group), and South Westland near Paringa (Tauperikaka Coal Measures; Nathan, 1977; Adams and Newman, 1987). These coals lie outside the area of study (Figure 1.3), and have not been examined by the writer.

Small areas near Inangahua contain coal of Miocene age (Rotokohu Coal Measures; Johnston, 1987), which occurs in workable quantities in a few localities although the total reserves are small. Stratigraphically equivalent coals occur further east, in the Murchison Basin (Longford Coal Measures).

1.4.2 Stratigraphy and distribution of Paparoa Coal Measures

The Paparoa Coal Measures comprise sediments of late Cretaceous (Haumurian) to Paleocene age, chiefly restricted to a northeast-southwest trough approximately 15 km wide. The trough is sited on a linear tectonic structure (Paparoa Tectonic Zone) which experienced incipient rift zone formation during Paparoa Coal Measures deposition. Persistent block faulting and central graben subsidence has resulted in a relatively narrow trough in which sedimentary units commonly thin rapidly toward the margins. Subsequent uplift, eversion, and erosion have reduced the coal measures to a large, southwest-dipping remnant at Greymouth and a smaller outlier at Pike River Coalfield.

Greymouth Coalfield. The stratigraphy of the Paparoa Coal Measures within the Greymouth Coalfield (Figures 1.5, 1.6) is complicated by both evolving basin morphology and local variation caused by uneven basin subsidence. Four fluvial coal measure units are broadly separated by three intervening lacustrine mudstone units.

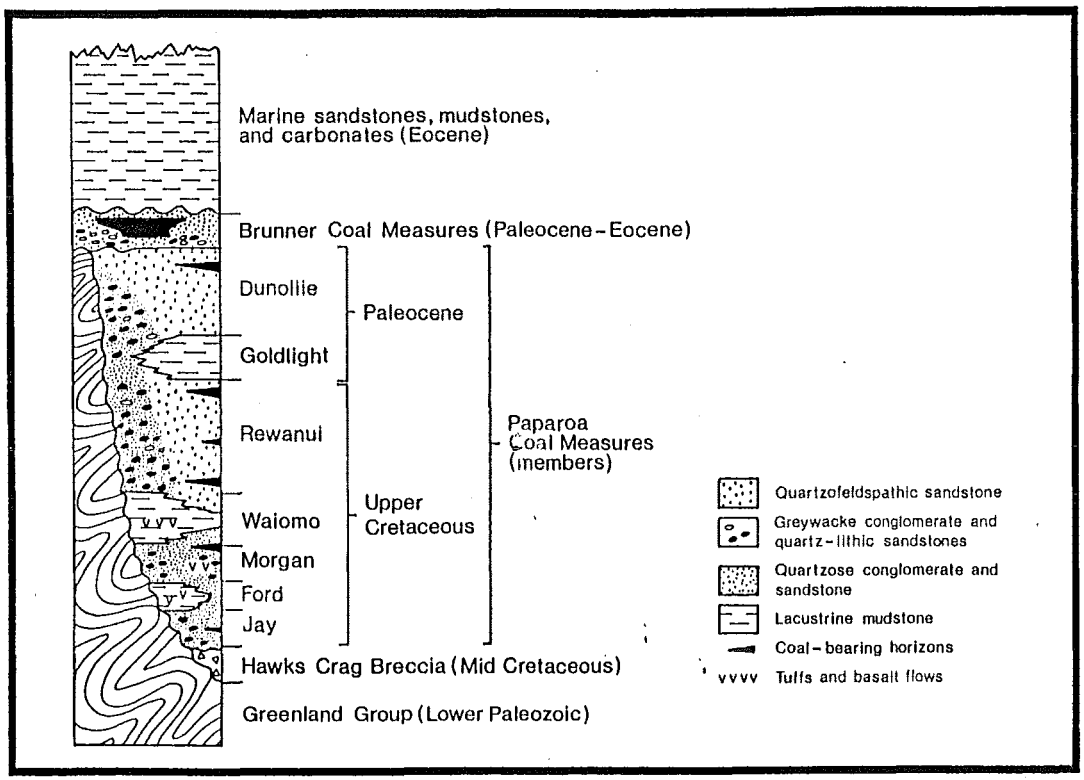


Figure 1.5 Stratigraphy of coal measures at Greymouth Coalfield. Adapted from Newman, J (1987, Figure 3).

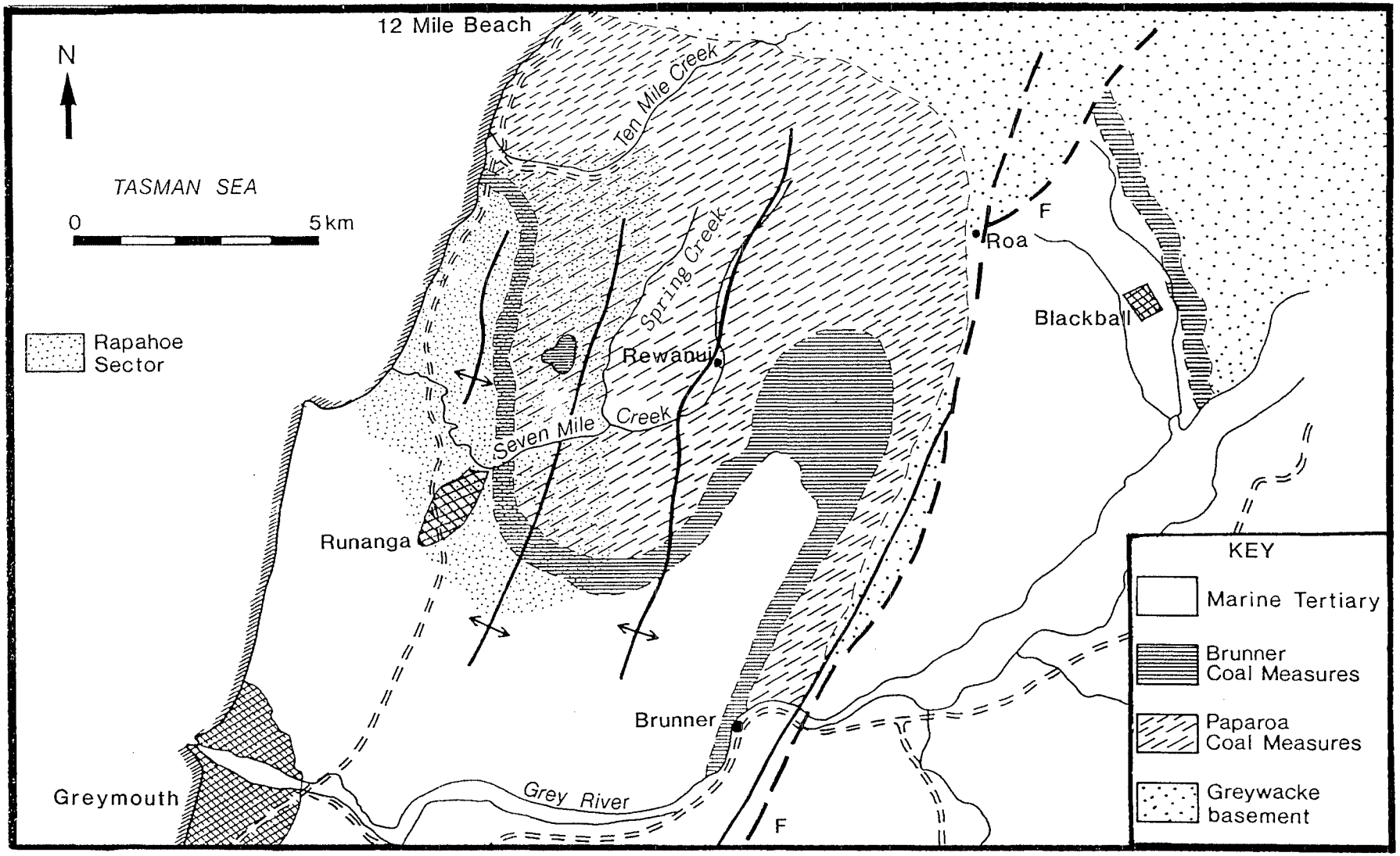


Figure 1.6 Greymouth Coalfield, showing simplified geology and localities mentioned in the text. Adapted from Newman, J. (1987)

The lowermost coal measures (Jay Coal Measures Member) and the overlying Ford Mudstone Member are considered to have accumulated in several small sub-parallel troughs or valleys orientated northwest-southeast (Gage, 1952). The Jay Member comprises a thick breccia sequence overlain in turn by conglomerates with minor sandstones, and a relatively thin coal bearing unit containing carbonaceous shale, sandstones and minor conglomerate.

Some of the breccia originally included in the Jay Member by Gage has subsequently been shown by pollen dating to be mid-Cretaceous Hawk's Crag Breccia (Nathan, 1974), and therefore cannot be included in the Paparoa Coal Measures. Despite this chronostratigrapic break, the overall sequence up to and including the Ford mudstone represents a gradual filling-in of old topography by talus debris, development of small and probably isolated fluvial systems, and gradual inundation by lakes due to central subsidence. The Jay Member is not known to contain workable seams.

Quiet impondment during deposition of the Ford Mudstone gave way to renewed fluvial deposition with the onset of Morgan Member sedimentation. Local uplift of source areas caused sand and conglomerates to cover and extend beyond the former Jay-Ford basins, and Morgan isopachs (Gage, 1952) indicate a gradual change in basin tectonics toward a new, northeast-southwest trough orientation which persisted throughout the remainder of Paparoa Coal Measures deposition.

In addition to conglomerates, sands, and silts derived from the regional Greenland Group basement, the Morgan Member contains locally abundant volcanic debris in the northeast of the coalfield. South of Roa (Figure 1.6), Morgan volcanics achieve a thickness of more than 450m, and comprise subangular to subrounded conglomerates with clasts of mainly basalt and lamprophyre, and lenses of tuffaceous sand and silt. Some basalt flows and pillow lavas are also known.

An active volcanic source at or immediately east of the basin margin near Blackball is envisaged, but no direct evidence of this feature remains. Extensive distribution of volcanic tephra took place during Morgan time, and an additional centre in the Spring Creek area is indi-

cated. Sparse tonsteins, interpreted as kaolinitised ashfalls are known from Morgan coals at Rewanui and Twelve Mile Beach, but ashfall evidence is unlikely to be preserved within the fluvial sediments. Volcanic activity was not restricted to Morgan time; tuffs have been found in the underlying Ford mudstone, and at many horizons within the overlying Waiomo mudstone.

Laterally persistent coal seam development at the top of the Morgan Member signifies the onset of tectonic quiescence which continued during deposition of the overlying Waiomo Mudstone Member. Lake waters inundated the Morgan peat swamps, and deposited a thin but very extensive area of mudstones and laterally equivalent sands and silts.

The succeeding Rewanui Coal Measures Member is distinct from the other fluvial members in several respects. It is a unit dominated by thick beds of flood-sheet and channel sands, silts, and conglomerates, and contains thick but often discontinuous coal seams at several horizons. In contrast to the older units, the Rewanui Member contains a large proportion of granitic debris. A complex pattern of sedimentation has resulted from the influence of differential compaction and basin faulting on fluvial drainage location. Areas which were persistently channel-dominated tend to contain thin coal, or high ash coal, whereas adjacent areas where sediment transport was infrequent often contain thick seams of workable coal (Newman, 1985a). Drilling funded by the New Zealand Coal Resources Survey programme has delineated an area where the Rewanui Member contains substantial deposits of unexploited coal, extending from Ten Mile Creek to south of Runanga, and termed the Rapahoe Sector (Figure 1.6).

Continued trough subsidence and declining source area uplift at the end of the Rewanui episode brought a return to lacustrine deposition and accumulation of the Goldlight Mudstone Member. Quiescent lake-margin conditions favoured development of some relatively extensive seams.

The final Paparoa Member to be deposited, the Dunollie Coal Measures Member, is of fluvial origin but contains a large proportion of fine-grained and compositionally mature sediment in comparison to the

other coal measure members. This evidence, and the widespread occurrence of extensive, evenly bedded, muddy overbank sequences, indicate a low rate of basin subsidence and low relief source areas. The prevalence of widespread, low energy flooding apparently proved unfavourable for persistent peat development, and workable Dunollie coals are restricted to a small area in the southwest of the coalfield.

Pike River Coalfield. Pike River Coalfield is an elongate remnant of Paparoa Coal Measures, some 1 km wide and 6 km in length, located at high altitude approximately 30 km north of Greymouth. The coalfield has been explored under licence by a private company, and is not included in the exploration programme of the New Zealand Coal Resources Survey.

Paparoa Coal Measures at Pike River exhibit a lithostratigraphy generally similar to the sequence at Greymouth, although the thick mudstone units are absent. Because there is insufficient evidence for direct correlation between the two coalfields, the nomenclature of Newman (1985a) is used to identify Pike River lithostratigraphic units (Figure 1.7).

Basal units comprise sporadic deposits of poorly rounded conglomerate of uncertain age (Member 1), resting on either Greenland Group or an erosional surface of mid-Cretaceous rocks, and commonly overlain by

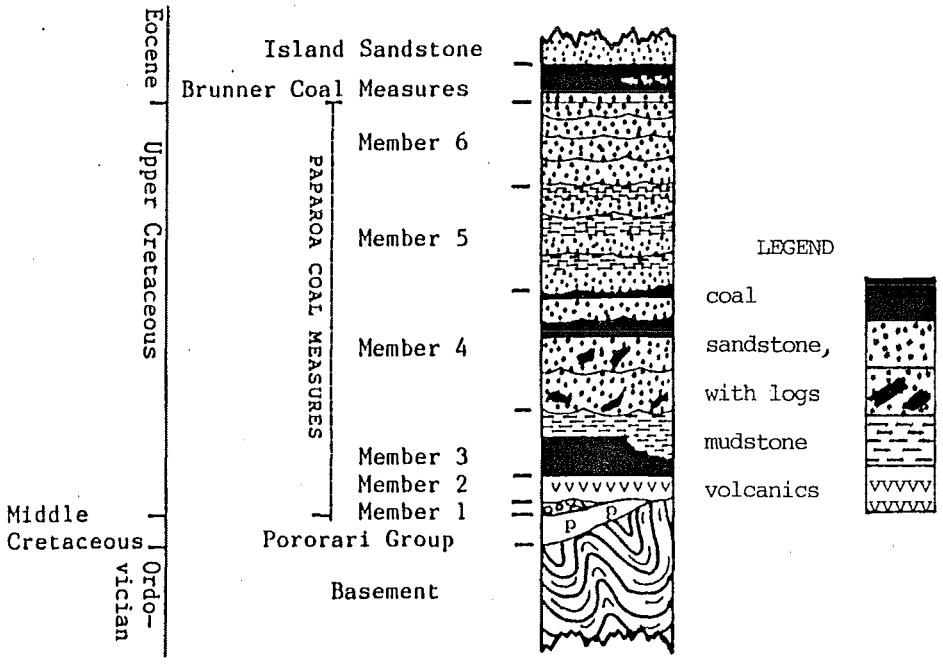


Figure 1.7 Diagrammatic stratigraphic column for Pike River Coalfield. Not to scale. Adapted from Newman, J. (1985a).

basaltic flows, aggregate, and tuffs (Member 2). The volcanic deposits grade upward into carbonaceous mudstone, coal, and minor sandstone, which are classified as Member 3. The Member 1-3 sequence bears an overall similarity to the Greymouth Jay-Waiomo sequence, although generally thinner and without major lacustrine mudstone deposits. Large and irregular thickness variations are attributed by Newman (1985a) to a combination of basement topography and syndepositional faulting. Member 3 coals also reflect this thickness variation, and are commonly high ash (> 10%), often containing mudstone partings and occasionally grading laterally into carbargillite. The Member 3 depositional environment is envisaged by Newman to represent peat accumulation in swampy depressions on a poorly drained post-volcanic terrain. Peat flooding by sluggish streams was common. Some of the earliest Member 3 peat accumulated during the final stages of volcanic activity, as shown by interbedding of tuffs and coal, and the formation of tonsteins.

Member 4 represents an abrupt change to distinctly fluvial deposition which can be compared with the Rewanui Member at Greymouth. Thick lenticular beds of granular sandstone and conglomerate of mixed Greenland Group and granite origin occur, occasionally accompanied by interbedded siltstone, mudstone, and coal. Member 4 coals are thinner, more extensive, and of lower ash than those of Member 3. Roof scouring is common in Member 3 seams, causing irregular thinning and frequent washouts.

Overlying Paparoa units (Members 5 and 6) are similar to Member 4, but are generally more evenly bedded and do not contain coal. These members represent chiefly extensive flood sedimentation and can be compared with the Dunollie Member at Greymouth. Members 4 to 6 undergo rapid lateral variation in thickness and lithofacies, attributed to differential subsidence during deposition.

1.4.3 Stratigraphy and distribution of Brunner Coal Measures

Brunner Coal Measures are widespread throughout the West Coast region, where they accumulated in response to a gradual marine transgression. Some thick Brunner sequences accumulated in subsiding

troughs, but elsewhere the coal measures are thin and locally absent on basement highs (Figure 1.8). Away from the subsiding basins, Brunner coals attain only sub-bituminous rank, in response to shallow burial by Tertiary strata. In the axes of Tertiary basins, however, Brunner coals have coking properties.

Brunner coal commonly occurs as a single seam, although a sediment split or rider seam is often present. However, in the Reefton area and at Buller Coalfield (Westport), several Brunner seams may be present, although the basal seam is commonly the thickest.

Suggate (1950) showed that Brunner Coal Measure sedimentation was ended by marine transgression, which slowly progressed from south to north. Further work, summarised by Nathan et al. (1986), shows a similar but more complex regional initiation of Brunner sedimentation, with some Paleocene accumulation at and south of Greymouth (Figure 1.9). In the centre of Greymouth Coalfield, Brunner Coal Measure chronostratigraphy is complicated by an early-mid Eocene hiatus of some 8 M. years. This break separates Paleocene from Eocene coal measure accumulation and appears to be located within a thick Brunner seam in at least one Greymouth locality. Such a hiatus implies an immense span of time, in terms of swamp history, of either nil or extremely slow peat accumulation (Newman, 1985a). The late Paleocene-early Eocene was a period of particular tectonic quiescence on the West Coast. The time represented by specific Brunner seams is very difficult to determine in many areas due to poor recovery of palynomorphs from Brunner coal.

1.5 PREVIOUS WORK

The principal literature of West Coast coal geology has been cited above. Relevant geochemical work can be subdivided into three categories, i.e., major element inorganic geochemistry (as ash constituent studies), trace element studies, and mineral matter studies.

Several workers have presented brief reports on West Coast ash constituents, but no detailed study has been attempted. Gage (1952) included representative analyses for the Greymouth coals, but did not

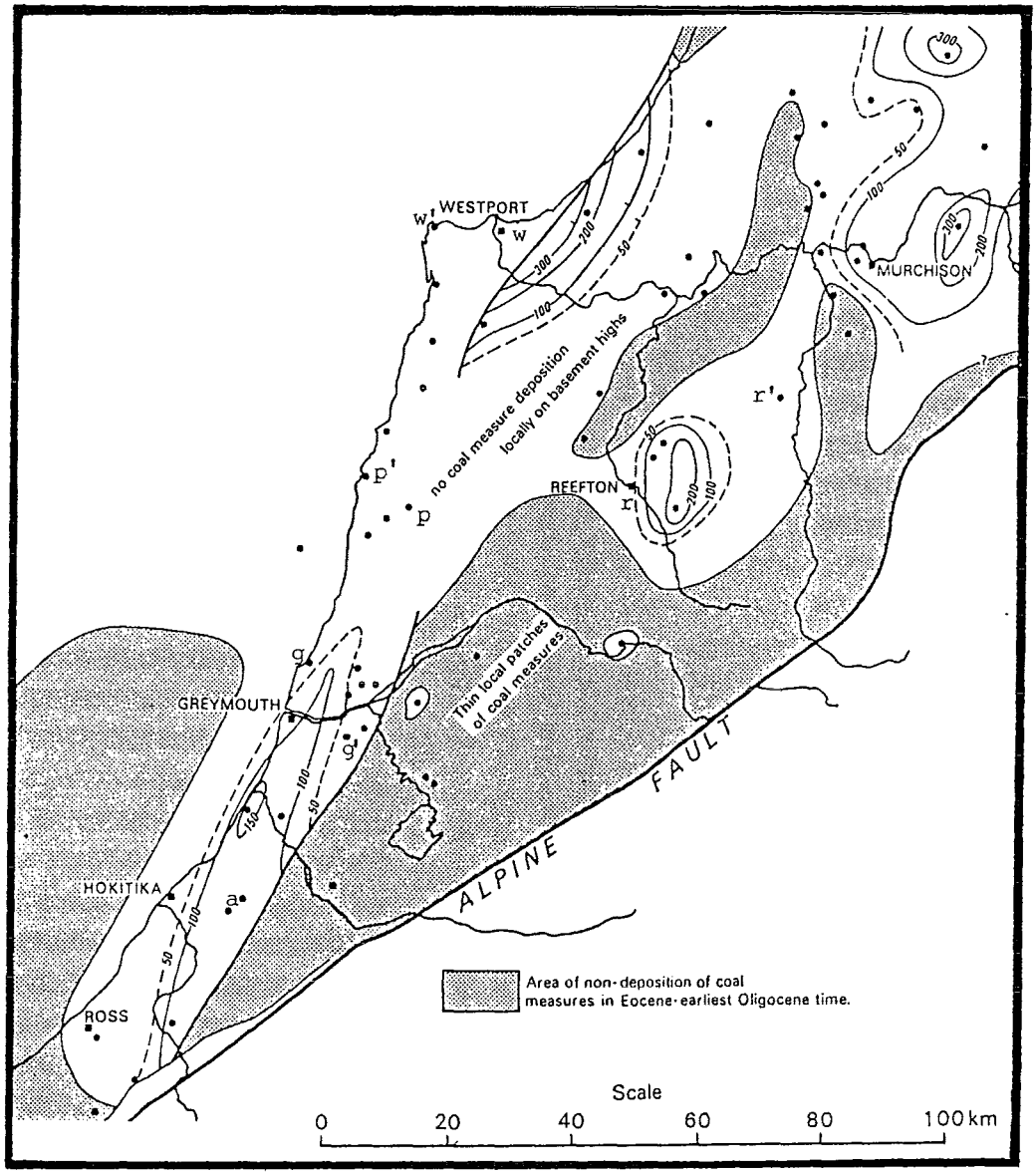


Figure 1.8 Original distribution of Brunner Coal Measures, Central West Coast Area. Isopachs in metres. (Adapted from Nathan et al. 1986).

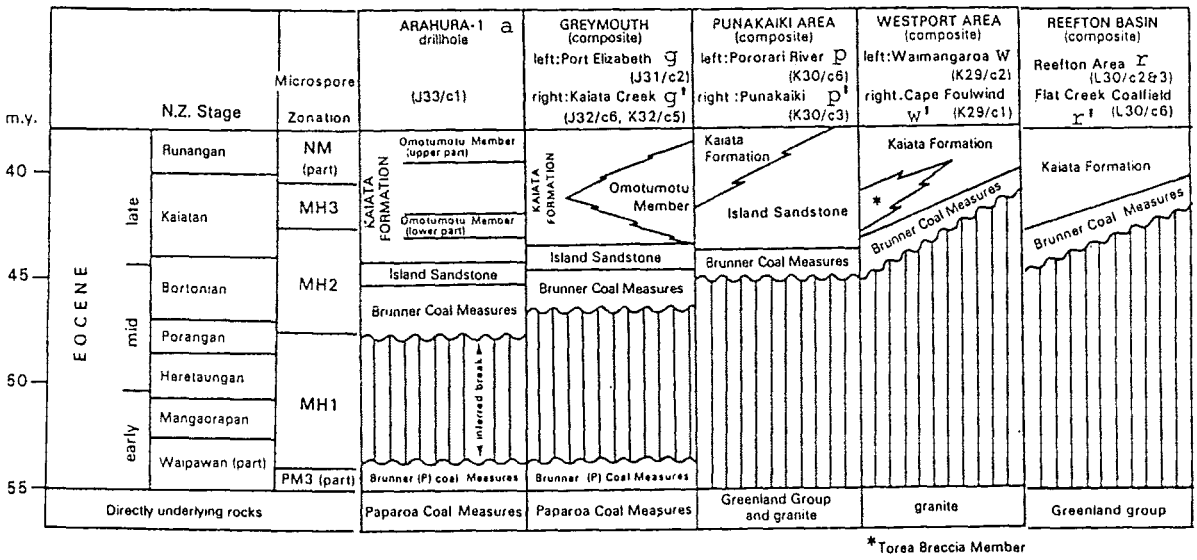


Figure 1.9 Chronostratigraphic correlation for Brunner Coal Measures and overlying units, principal West Coast Coalfields. (Adapted from Nathan et al., 1986). For section locations see Figure 1.7 (g - g' etc).

discuss their significance. Similarly, Hughson (1953) presented a few representative analyses, but limited his discussion to ash fusion temperatures. Bowden and Roberts (1975) listed incomplete ash analyses for all major West Coast working mines, and attempted to correlate the data with ash fusion temperatures. Of greater significance to the present study is the work of Soong and Berrow (1979), which included ash analyses for four West Coast coals, and an attempt to relate some compositional trends to known mineral suites.

At various times, West Coast coal samples have been analysed for certain trace elements, but with little or no interpretation of the data. Boron and strontium levels were briefly reported by Rafter (1945), and a more comprehensive treatment of boron presented by Kear and Ross (1961). Values for a wide range of trace elements were given by Sim and Lewin (1975), Sim (1977), and Soong and Berrow (1979). Fluorine values for four West Coast coals were determined by Soong et al. (1984), and all trace element data have been the subject of a critical review by Purchase (1985). More recently, a small number of ash constituent analyses were carried out for Rotokohu coals from the Inangahua area by Johnston (1987), and for Upper Cretaceous and Eocene coals in South Westland (Adams and Newman, 1987).

There is very little previous work dealing with West Coast mineral matter. Gage (1952) made a few observations, and Suggate (1959) briefly considered the subject when determining correction formulae for proximate analyses. Budge and MacKnight (1976) provide a useful table of forms of sulphur data which includes 38 West Coast coals, and the work of Soong and Gluskoter (1977) provides direct mineral matter analyses for four West Coast samples, together with some discussion and interpretation. Gray (1981) discussed minerals in Buller coals, drawing upon a report by Gaigher (1981), who undertook some mineral matter analyses of New Zealand coals in general. Some further data and interpretation for minerals in Buller coals appear in a report by Sheat (1984), and numerous references to mineral matter seen in polished section are to be found in the thesis by J Newman (1985a). Some details of mineral matter in the Rotokohu coals have been discussed by Johnston (1987).

1.6 RESEARCH DESIGN AND HISTORY

An important prerequisite for any study involving coal microscopy is an adequate understanding of coal petrography. Prior to the commencement of research, the writer took an opportunity to study this subject at the Department of Geology, University of Wollongong, where tuition and facilities were made available by Professor A.C. Cook.

Subsequently, the course of research has been influenced by two important factors, as follows:

(i) The work by J. Newman (1985a).
Much of the sample collection and field observation work was undertaken during periods when the writer assisted Dr Newman with fieldwork. Futhermore, Dr Newman's work has provided a substantial suite of polished coal sections. Assistance received from Dr Newman by way of advice on petrographic description and paleoenvironmental interpretation is duly acknowledged in the text.

(ii) Coal exploration.
During early stages of the research, little drillcore material was available, and a large proportion of the sample collection was obtained from outcrop or old workings. Later in the course of this project, however, substantial coalfield drilling and exploration programmes were carried out. The Ministry of Energy Coal Resources Survey funded drilling at Greymouth, Garvey Creek, and Buller Coalfields, and a private company explored and drilled the Pike River Coalfield. Comprehensive core logging, downhole logging, and sample analysis in the course of these programmes has resulted in an enormous increase in the West Coast coal database and sample availability.

Many excellent suites of coal core samples have been studied in preference to the earlier surface samples, most of which are partially weathered and have no corresponding proximate analyses. In some cases later work has effectively duplicated earlier analyses, but has provided better data.

Samples were selected both to obtain representative data for whole seams or localities, and to investigate more detailed mineral and chemical trends within individual deposits. To fulfil the requirements of the latter, particular attention was given to obtaining some sets of thin plies (< 1m) and avoiding contamination.

Initially, analysis of a wide range of trace elements by X-ray fluorescence (XRF) was anticipated, but despite substantial developmental work and sample preparation, this programme was eventually abandoned in favour of additional major element and mineralogical work. This change of direction was prompted by difficulties involving contamination levels relative to detection limits, and the problems of obtaining suitable calibration. Furthermore, after a survey of the literature of of trace elements in coal, there appeared to be little scope for satisfactory interpretation of such data unless the geochemistry of the major elements, and their mineralogical occurrence, were known.

Preliminary indications from the trace element work suggested that West Coast coals exhibited generally low values for most trace elements, relative to overseas coals, as previously reported by Sim (1977). This factor aggravates problems of sample preparation and contamination.

XRF has been used to analyse the conventional range of major elements, and Sr and Ni, in coal ash, and Ba in whole coal. Analysis of Sr and Ba was undertaken to investigate the degree of substitution in phosphate and carbonate minerals. Analysis of Ni was added to the analytical programme set up for Sr, because it was found that a satisfactory response for Ni could be obtained from the fused disk samples already prepared. Although this project is not primarily oriented toward trace elements, it was considered worthwhile to include the Ni data in the tables and the discussion, particularly as Ni is an element of potentially high organic affinity (Gluskoter et al. 1977), in contrast to most of the major elements.

Mineralogical analysis has been relatively straightforward. Mineral matter residues from a low temperature asher have been analysed, mainly by X-ray diffraction. Personal computers were made available in 1985, and have greatly assisted the processing and interpretation of analytical data.

CHAPTER 2

METHODS

2.1 SAMPLING

Sample collection was very much dependent on the availability of suitable material at the time when the project was undertaken; special efforts were made to coordinate with other workers or organisations who were working with West Coast coal samples. Other material was collected from outcrop, old mineworkings, stockpiles, and working mines (Table 1.4).

A very wide range of sample type is represented, ranging from carefully logged and analysed plies from drillcore to "grab" samples collected from spilled coal lying about the portals of old workings. Because small-scale mining has taken place on the West Coast for more than a century, each major coalfield contains a large number of abandoned mines. For example, Gage (1952) listed 100 individually defined mines for the Greymouth District. Of these, only two (Strongman and Liverpool) remained working when samples were collected for this project. Most old workings are now inaccessable, although in a few cases safe entry is possible. At many abandoned workings, reasonably fresh coal can be obtained from old bin sites, dumps, etc., although there is no direct evidence of where the sample originated with respect to location in the mined seam, or seams.

Narrow ply sampling, where practical, is considered to be important because a coal seam is the compressed remains of a peat swamp which probably underwent both gradual change and a series of rare events (dehydration, flooding, sedimentation, ashfalls, etc.). Samples of full-seam

thickness will tend to average the effects of these events, and run of mine coal will combine the effects of lateral variation as well. In the case of particularly low ash seams, which are common in the West Coast region, one or more sediment-rich horizons, which collectively may represent a negligible fraction of total swamp history, may completely mask the geochemical character of the remainder of the seam. Although low ash coal can be isolated from such samples by gravity separation, much information remains lost by the mixing of different horizons.

Where the tables show sample details, sample type (as distinct from coal type) is indicated by a suitable abbreviation, indicating channel samples, run-of-mine samples, spot samples etc. Where mine names are quoted, care has been taken to avoid confusion arising from the frequent re-use of names at different localities. Samples not collected by the author were supplied by Coal Research Association of N.Z. (CRA) on request.

In addition to the coal samples listed in the tables, a small suite of non-coal lithologies were selected for mineral and chemical analysis. These sediments, which were obtained from both outcrop and drillcore, comprised several lacustrine mudstones from the Paparoa Coal Measures, and various partings and floor rocks from coal seams.

2.2 SAMPLE PREPARATION

Preparation methods are summarised in Figure 2.1. Field samples were air dried and stored in labelled bags until analysis, when they were pre-crushed to approximately pea-grade by means of a jaw crusher set for ¼" (6.3 mm) gap. Small samples were crushed by hand in a mortar.

If necessary, the crushed sample was then split to provide a subsample not exceeding 250 gm. If a petrographic split was to be retained, the entire subsample was processed by incremental screening and grinding with a coffee grinder, to provide -1 mm sizing with minimum overbreakage.

A similar procedure was carried out for samples supplied by CRA, which provided splits from the original bulk sample, nominally crushed to -¼" (-6.3 mm). However, it is important to note that due to worn equipment, some CRA samples contained particles with a minimum dimension exceeding 10 mm. This may seriously degrade representation of the bulk sample, by failing to maintain an adequate topsize - minimum increment relationship. The effect of poor representation by these samples will not seriously affect the inferences and interpretations developed in this work, but may be the principal cause of occasionally poor agreement between results obtained by the writer and those from other laboratories, where a direct comparison is possible.

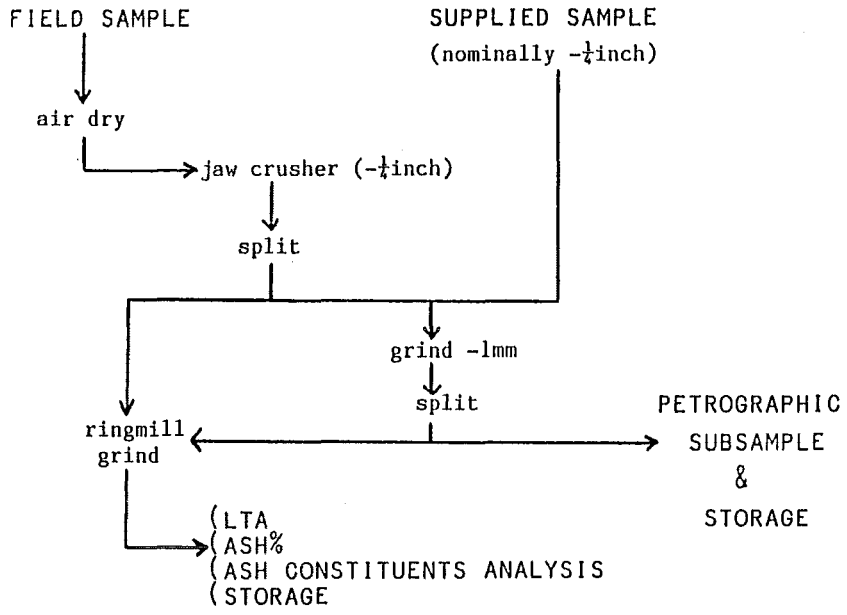


Figure 2.1 Sample preparation procedure.

Following coarse grinding and splitting, fine grinding was carried out by pulverising for 30 seconds in a ringmill, to yield a powder which was stored in sealable jars or plastic bags. All sample weighings were made on an "air dried" basis, which refers to equilibrium with laboratory conditions. Temperature variations about a mean of 20°C were small, but no humidity control was possible. Because the West Coast samples studied are almost entirely of bituminous rank, errors due to the lack of a controlled atmosphere are considered negligible. In any case such errors would effect only the determinations of total ash and total mineral matter.

Some samples were separated into specific gravity fractions by the use of perchloroethylene - petroleum spirit mixtures. The densities were chosen to provide a wide range of fractions for analysis.

2.3 MINERALOGICAL ANALYSIS

2.3.1 Low Temperature Ashing

Mineral matter was isolated by the use of a radio frequency (RF) plasma asher, model LTA 304(2) manufactured by LFE Corporation, Waltham, Massachusetts. This machine has two chambers, each of 4 inches (100 mm) internal diameter, and a somewhat generous total power capacity of 300 watts. Operating conditions were 40 watts power and 175 ml/minute oxygen flow, per chamber. Oxidation temperatures were typically 130-140°C, as determined by measurements of sample temperature with an infra-red thermometer, via a halide window fitted to the ashing chamber (Appendix I). Two or three samples were ashed simultaneously in each chamber, oxidation usually taking 12-24 hours to complete. All except very low ash coals required stirring after the first few hours oxidation. On completion of oxidation, the residues were either processed directly for mineralogical analysis, or weighed and stored in sealed phials for later analysis.

Records of low temperature ash % were kept, but these data are considered misleading and have not been listed in this work. The generally low yield of LTA aggravated errors due to sample hydration, and many high sulphur coals could not be oxidised to completion, due to the accumulation of sulphate in the sample material.

2.3.2 XRD Procedure

The principal difference between this study of mineral matter and similar studies carried out in Australia, South Africa, North America, and Europe, is the comparatively low mineral matter content of the West Coast coals. This characteristic imposed a limitation on the range of practical analytical procedures. Mineral analysis by XRD of whole coal, as demonstrated by Mitra (1964) and Gaigher (1980), suffers from low sensi-

tivity, and this option was even less attractive in the absence of a beam monochromator and sample rotator. To obtain sufficient mineral matter from all samples to prepare conventional cavity mounts and satisfactory clay mineral fractions would have required a substantial increase in average oxidation time. Because of these difficulties, and in view of the large number of samples to be processed, a simple slurry-on-glass slide technique was adopted as standard procedure for whole mineral matter analysis.

Initial trials with alcohol, acetone, and water slurries produced poor results due to the presence of soluble material in the LTA residues; compounds synthesized during or after oxidation obscured the mineral patterns with additional peaks and high background scatter. To overcome this problem, the residues were washed with distilled water as follows. Sufficient LTA residue was placed in a small agate mortar and ground briefly in water to produce a slurry. The mortar was then filled with distilled water and the contents mixed thoroughly, after which the solids were allowed to settle out of suspension. Most of the water was then removed with a syringe, and the washing process repeated. The solids were then carefully ground to produce a uniform, thick slurry. A portion of this was transferred to a glass slide, spread into a layer of even thickness, and allowed to dry. This produced a sample density of approximately 1.5 - 1.7 $\mu g/mm^2$.

The sample mounts were analysed by a conventional Philips PW1050 diffractometer fitted with a proportional counter and pulse height discriminator. Generator settings were maintained at 34 kV and 34 mA supplied to a copper tube, and scan rates of 1°/minute were used throughout the work.

Where necessary, samples were re-analysed after supplementary treatment to assist mineral identification. These procedures included acid treatment to remove carbonates and sulphides, and glyceration - heating sequences to investigate clay mineralogy. In a few cases, a clay fraction was separated and treated to improve dispersion and orientation, by using a citrate-dithionate treatment similar to the method outlined by Ward (1977).

2.3.3 Semiquantitative Analysis

Mineral assemblages have been expressed in the tables in two forms:
(i) Relative abundance, by the use of "greater than" and "equal to" symbols.
(ii) Numerical percentage estimates of the principal silicate-related minerals (quartz, kaolinite, illite group, and boehmite) summed to 100%.

Conventional methods of quantitative mineral analysis employ whole-sample pack-mounts with an internal standard to estimate non-clay minerals, and sedimented or smear mounts of a dispersed clay fraction to estimate clay minerals. It is known that the use of simple slurry mounts for quantitative analysis may incur error as a result of differential settling, differential particle size effects, and variable orientation (e.g. Brindley & Brown, 1980). Further errors can be induced by inadequate dispersion, and by oxide coating of the clays (Ward, 1977).

Nevertheless, a useable calibration for the above "silicate-related" minerals has been obtained by preparing three series of binary mixtures from clay minerals extracted from the samples themselves. Standards of this type have advantages over mixtures of materials from external sources (Gibbs, 1967). The calibrations were devised as follows:

(i) Kaolinite plus illite. A series of standards were prepared by mixing almost pure kaolinite with illite containing minor kaolinite. Both components were obtained from mineral matter extracted from Buller coals. The regular curves obtained by measuring 7Å and 10Å peak intensities (Figure 2.2) are similar to the calibration advocated by Griffin (1971) and subsequently used by Ward (1977, 1978) and Gaigher (1980). Better control of the low-kaolinite region by the data points is obtained if a curve for I (7Å) kaolinite/ I (10Å) illite is plotted in addition to the more usual factor I (7Å) kaolinite/ I (7Å) kaolinite + I (10Å) illite. The term illite represents a group comprising illite and expandables, as discussed in Section 3.4.

(ii) Kaolinite plus quartz. As expected, this calibration (Fig. 2.3) is not so well defined as for the clay mixtures, because of differential

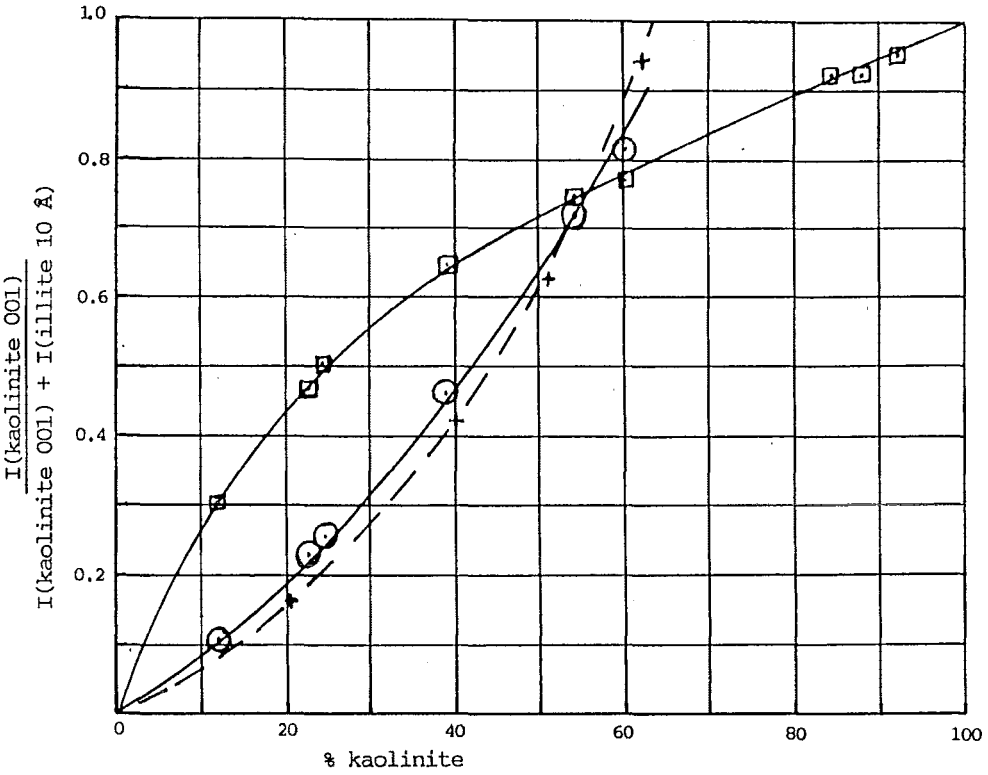


Figure 2.2 Kaolinite-Illite calibration graph.
⊡ Observed calibration for vertical scale as shown
⊙ Observed calibration using a vertical scale of $\frac{I(\text{kaolinite 001})}{I(\text{Illite 7Å})}$
\+ Calibration using the relationship of Griffin (1971), vertical scale as above.

particle size and shape effects (see above). Poorest control of the calibration curve occurs about the mid-point, and it can be shown that "thin" mounts tend to plot below the curve. Maximum error for the working curve is considered to be about ± 10% quartz. For comparison, a similar calibration used by Botz et al. (1986) for kaolinite-rich compositions is shown, recomputed for quartz 100 reflections using the 100/101 relationship shown below.

(iii) Kaolinite plus boehmite. A relatively pure sample of boehmite isolated from Greymouth coal was mixed with kaolinite to provide calibration mixtures. Seven data points provide a smooth curve (Figure 2.4).

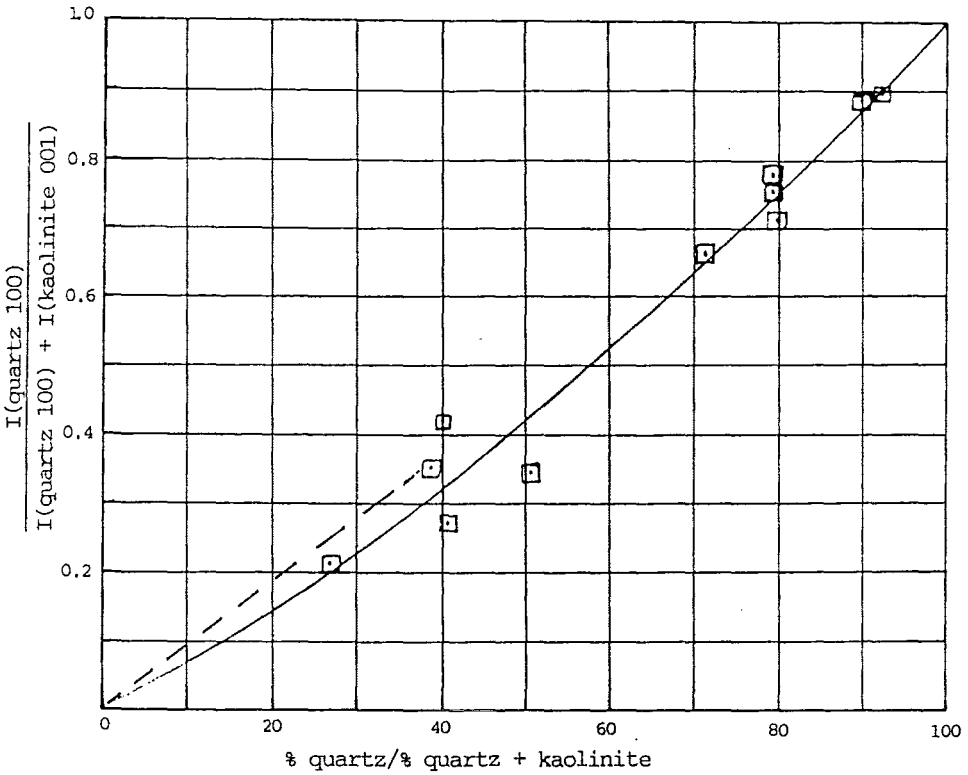


Figure 2.3 Kaolinite-quartz calibration graph. Dashed line = relationship observed by Botz et al., (1986).

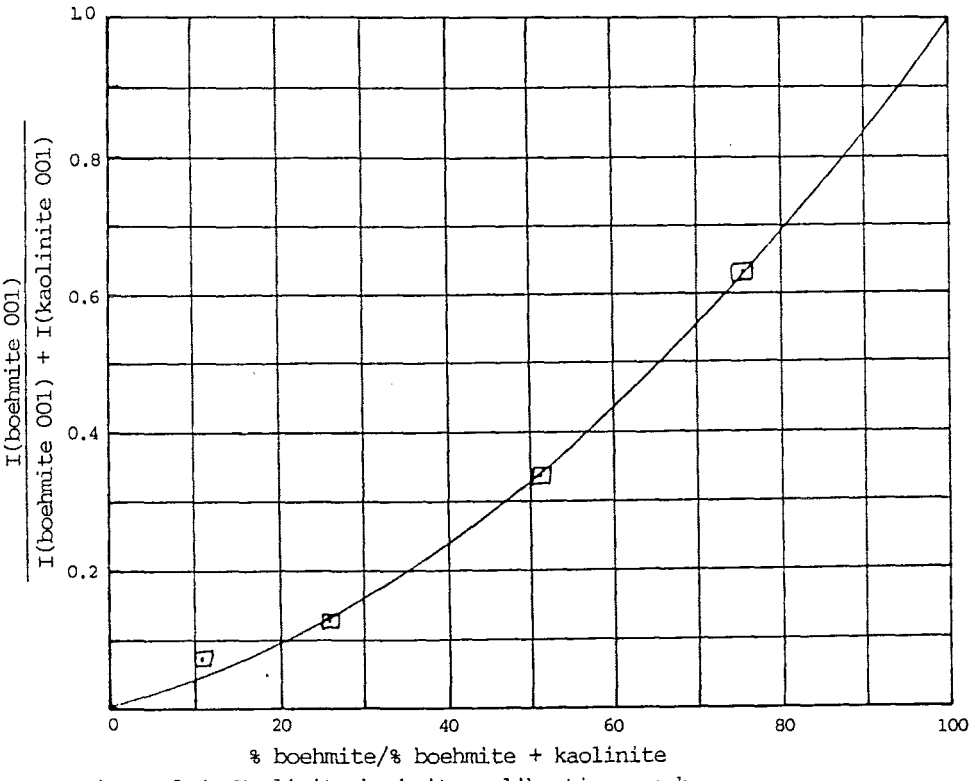


Figure 2.4 Kaolinite-boehmite calibration graph.

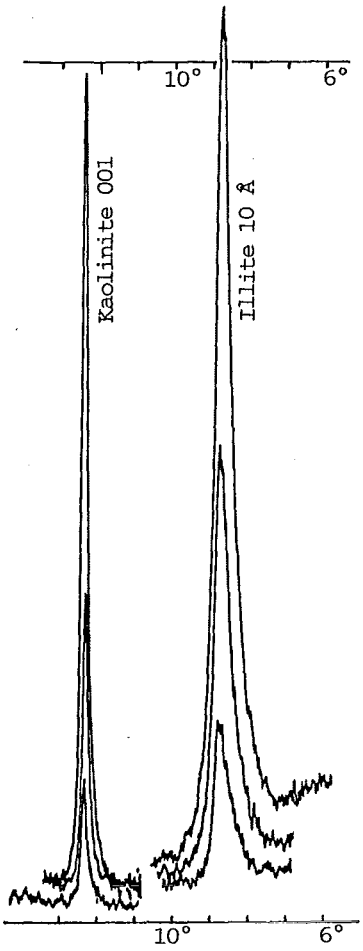


Figure 2.5

Family of peak shapes produced by differing abundances of standard kaolinite and illite in calibration mixtures.

The calibrations were all determined using peak intensity, as opposed to the peak area relationships favoured by clay mineralogists. Errors due to this simplification were minimised by preparing a set of peak shape tracings for the calibration minerals (Fig. 2.5), and applying compensation where a significant shape mismatch occurred. This chiefly affected the illite group, and to a much lesser extent, kaolinite.

The results obtained by the use of these techniques should be regarded as semiquantitative, especially with respect to quartz. The calibration is specific to the method of sample preparation adopted for this work; other workers may need to erect their own calibrations if using slurry mount methods. Furthermore, it must be emphasised that the method estimates total quartz and clays, not just the -2μ clay fraction.

It is notable that the clay mineral results appear unaffected by sample thickness in slurry mounts, in contrast to the marked thickness-

dependence demonstrated by Gaigher (1980, Figure 3), for sedimented illite-kaolinite mixtures. Errors due to inadequate dispersion, variable orientation, and variable sample thickness are minimised by using closely-related d-spacings for each mineral pair, e.g., primary basal spacing for illite, kaolinite, and boehmite, and quartz 100 and kaolinite 002 for quartz-kaolinite. Where these peaks could not be used (e.g., due to interference), alternative peaks were selected using the following observed mean relationships:

Kaolinite 002/001 = 0.56; quartz 100/101 = 0.22.

During the calibration procedures, intensity ratios of the illite-kaolinite and quartz-kaolinite pairs were tested in the presence of other minerals. There was little effect when minerals of the specified "silicate-related" group were mixed, but poorer reproduceability occurred in the presence of large proportions (> 50%) of carbonate minerals, gypsum, and pyrite. These tests were also used to provide a basis for expressing the nonsilicate minerals in terms of relative abundance. Although carbonate abundance can be expressed with some confidence, results are poor for pyrite and gypsum. For reasons discussed below, gypsum has been excluded from the mineral-abundance data.

LTA from three run-of-mine coals was prepared and analysed for -2μm kaolinite, illite, and expandable clay, by the method described by Ward (1977). These data, which cannot be directly compared with results from whole LTA, are discussed in Chapter 8.

2.4 OTHER MINERALOGICAL METHODS

Some coal samples with a high iron content were analysed by Mössbauer spectroscopy at the Department of Physics, University of Canterbury, by Mr Q. Pankhurst and Dr V.H. McCann. The full results of this work are presented in a separate publication (Pankhurst et al., 1986; Appendix 3, this work), and relevant details incorporated in this thesis where appropriate.

Polished sections were examined with a Leitz Ortholux relecting microscope, fitted with a Leitz Vario-Orthomat camera. This equipment

was used to obtain most of the photographs shown in this work. Some Scanning Electron Microscopy was also used.

2.5 CHEMICAL ANALYSES

For measurement of percentage high temperature ash, and to provide ash for XRF analysis, coal samples were ashed in silica crucibles in an electric furnace. The procedure followed was similar to that specified in BS1016 Pt 3 (Proximate Analysis of Coal) with a final temperature of 815°C. The only significant departures from the standard method were sample layer thickness (exceeded 0.15 gm/cm^2), and furnace ventilation (not measured).

For a selected range of coals, ash constituent (major element) analysis was performed using a conventional XRF technique based on the fused disk method developed by Norrish and Hutton (1969), and later modified by Harvey et al. (1973). Prepared disks were analysed on an automatic Philips PW1400 XRF, from which the data output was corrected by on-line computer. Disks prepared from international standard rock powders were used for calibrating all major elements except sulphur, for which artificial standards were used.

A small number of barium determinations were carried out by XRF of whole coal, using an internal mass absorption correction based on known concentrations of titanium, which provides a fluorescence line (Kα, 2.75Å) which is very close to barium Lα (2.77Å). The technique used international standard rock powders for calibration and was checked against an international standard coal (SRM 1632a).

Strontium and nickel were measured in high temperature coal ash, by analysing Norrish-Hutton fused disks by XRF, in combination with a conventional Heinrich mass absorption correction based on major element analysis. Fused disks from international standard rocks provided the calibration.

All analyses were carried out by the author unless otherwise stated.

2.6 COMPUTED MINERAL ASSEMBLAGES

2.6.1 Introduction

In view of the difficulties involved in successfully carrying out full mineralogical analysis for a large number of low ash coals, efforts have been directed towards devising a method of computing mineralogical compositions from major element analyses. This would permit statistical treatment of the large number of existing analyses for West Coast coal samples, and would provide a readily applicable method of obtaining mineral matter/ash factors for individual samples, allowing improved correction of major coal characterisation parameters.

Calculation of coal mineralogy from chemical analyses of ash has been carried out sporadically over many years, but only the more recent attempts have had the benefit of XRD characterisation of the true mineral assemblages (Rao and Gluskoter, 1973; Ward, 1977; Pollack, 1979; Given et al., 1980). Most of these authors describe the method as "normative analysis" by analogy with the similar method used for igneous rocks. However, this term implies a fixed mineralogy which may not be represented in the sample, whereas the authors cited were attempting to quantitatively assess the actual coal mineral assemblage. A major problem affecting these attempts to compute mineralogical composition is the use of a single formula for samples from a very wide area, in some cases spanning more than one coalfield.

The computation procedure adopted for West Coast coals incorporates the following improvements over previous schemes:

(i) A larger number of mineral phases is calculated.

(ii) Different formulae are used for each mineralogically distinct group of coals.

(iii) Mineral compositions are adjusted to incorporate characteristics inferred from XRD and other evidence.

Details of the computation scheme are given below, but the evidence on which it is based is contained in Chapters 3, 4, and 5.

2.6.2 Method devised for coals from Paparoa Coal Measures

(i) All P_2O_5 is assigned to crandallite, using an ideal formula $CaAl_3(PO_4)_2(OH)_5H_2O$. Crandallite composition is discussed in 3.10.

(ii) Illite is calculated by a single formula, $K_2O(SiO_2)_{5.5}(Al_2O_3)_{4.0}$ + 6%H_2O. This departs from the conventional assessments of illite composition, based on Fithian illite or "average" illite estimated from published analyses (e.g., Weaver and Pollard, 1973). For the above formula, K_2O is higher, and H_2O lower, than generally accepted compositions for sedimentary illites, and substituting cations (Na, Mg, Ca, Fe, Ti) are ignored. The formula corresponds to an ideal illite $K_nAl_4(Si_{8-n},Al_n)O_{20}(OH_4)$ in which n = 1.5, a value intermediate between typical soil and marine mud illites (n near 1), and muscovite (n = 2). On the basis of XRD peak morphology and compositional evidence, illite in West Coast coals is considered to have a strongly "sericitic" element, and in some cases may include a proportion of relatively unaltered muscovite. Application of the above formula to the Brunner illite selected as an XRD standard (sample B26) gives a calculated composition very close to that determined by calibration using known additions of kaolinite:
by XRD, illite = 89%, kaolinite = 11%, quartz = trace;
by calculation, illite = 89.1%, kaolinite = 10.6%, quartz = 0.3%.

However, it is clear that the composition of illite in the coals is variable. Many of the low-ash coals contain interlayered illite which is underestimated by the calculation method.

(iii) Kaolinite is calculated from the ideal formula, $(SiO_2)_{1.18}(Al_2O)_{1.0}$ + 14% H_2O.

(iv) Surplus SiO_2 is reported as free quartz. If surplus Al_2O_3 is present, it is reported as boehmite, and free quartz is considered absent. Because boehmite is an extremely rare mineral in Paparoa coals, it has not been allotted a column in the mineral tables, although its presence is indicated by zero quartz and its magnitude by (100%-total).

(v) Siderite is computed on the basis of total Fe_2O_3 in ash. The low abundance of pyrite in most Paparoa coals (e.g., Budge and Mac-Knight, 1976), and the paucity of other iron minerals support this assumption. However, certain Paparoa seams in the Rapahoe Sector, or areas within these seams, do contain appreciable pyrite and a correction should be made where forms of sulphur data are available. Unfortunately, these data are few in number, but an estimate of pyrite has been made on the basis of total sulphur, as outlined in 5.4.1.

MnO, MgO, and non-crandallitic CaO are considered to occur predominantly as carbonates. Plotting these oxides against Fe_2O_3 reveals a positive correlation for MnO and MgO, but a poorly defined relationship for CaO. The 'best approximation' procedure adopted for these oxides is to compute them all as their respective carbonates, and include all $MnCO_3$ and $MgCO_3$ in the siderite total. CaO is assumed to substitute FeO to a maximum of 10% of iron as Fe_2O_3 (i.e. approximately 9% FeO equivalent), and the surplus is reported as calcite.

(vi) All TiO_2 is assigned to rutile, the only titanium mineral identified in the coals.

2.6.3 Modifications for coals from the Brunner Coal Measures

(i) All the high rank Brunner coals contain significant amounts of boehmite, and this mineral is included in the Brunner tables and figures. However, partitioning of Al_2O_3 remains as outlined above; boehmite is calculated on the basis of surplus Al_2O_3 after calculating kaolinite. Dawsonite occurs in some Brunner coals at Greymouth Coalfield, but has been neglected from the calculations because only a few samples are affected. This omission can be expected to distort the computed aluminosilicate mineralogy of some Na_2O-rich Greymouth plies and spot samples, but could be remedied by assigning Al_2O_3 to dawsonite ($NaAlCO_3[OH]2$) prior to calculating illite. Similarly, a few coals from the Buller Coalfield are considered to contain significant amounts of K-bearing minerals resulting from recent weathering, probably jarosite, which causes overestimation of

illite and other problems. A correction for this effect requires separate determination of K_2O in sulphate extracts.

(ii) Siderite does not occur in Brunner coal, although ankerite is found in some of the coal at Flat Creek (Murchison). All Fe_2O_3 is assigned to pyrite (which incorporates marcasite), on the basis of evidence relating total iron to pyritic sulphur at Buller Coalfield, and the general absence of iron-bearing minerals other than sulphides. Traces of chlorite occur in some Brunner coals, but this mineral is sufficiently sparse to be neglected from the calculations. Error may result from weathering, where sulphides decompose to leave a residue of oxides; no estimation of this effect can be made unless forms of sulphur measurements are available.

(iii) Carbonate minerals are common in Brunner coals, where they occur as calcite and dolomite. The method adopted is to assign all MgO to ideal dolomite, and express surplus CaO (corrected for crandallite) as ideal calcite. MnO is neglected, because of the extremely low concentrations of this component, which shows no relationship with CaO or MgO.

CHAPTER 3

MINERALS IN WEST COAST COALS

3.1 INTRODUCTION

This chapter describes all major and minor minerals (excluding organically bound mineral matter and trace minerals) identified in West Coast coals. Details of mineral composition and terminology are given, together with brief descriptions of mineral occurrence and distribution, but a more complete discussion of mineral origins, composition, and relationship to ash chemistry is provided in later chapters.

A summary table from the earlier work of Soong and Gluskoter is reproduced below (Table 3.1) and may be compared with the more comprehensive summary of mineral identification and distribution generated by this work (Table 3.2).

	Sample (locality)	Rank	Quartz	Kaolinite	Illite	Gypsum	Anhydrite	Calcite	Ankerite	Siderite	Dolomite	Ammonium compound	Compound of nitrate	Compound of oxalate
1	Stockton*	Bituminous	C	A	R	-	C	-	-	-	-	A	-	-
2	Strongman*	Bituminous	A	A	R	R	-	-	-	C	-	-	-	-
3	Dauntless *	Bituminous	C	A	R	-	C	-	-	-	R	C	-	
4	Liverpool *	Bituminous	C	A	R	-	R	R	-	-	-	-	-	
	Ohai	Sub-bituminous	C	A	R	-	C	-	-	R	-	C	-	-
	Rotowaro	Sub-bituminous	C	C	R	C	R	R	R	-	-	-	C	R
	Renown	Sub-bituminous	C	A	-	C	-	R	C	-	-	-	C	R
	Kopuku	Sub-bituminous	A	C	R	A	R	R	-	R	-	-	A	R
	Pirongia	Sub-bituminous	A	C	R	-	C	-	-	-	-	-	-	-
	Wangaloa	Sub-bituminous	R	R	-	R	A	-	-	-	-	C	R	-
	Glen Afton	Sub-bituminous	C	C	-		-	R	-	R	-	-	C	R
	Wairaki	Sub-bituminous	C	C	-	-	C	R	R	-	-	-	C	R
	Waimumu	Lignite	R	C	R	-	C	-	-	-	-	-	C	-

* Mineral matter obtained by low-temperature ashing of coal
A Abundant C Common R Rare

Table 3.1 Mineral matter in New Zealand coals, adapted from Soong & Gluskoter (1977). *West Coast samples.
1 Brunner coal, Buller Coalfield 2 Paparoa coal, Greymouth Coalfield 3 Brunner coal, Reefton Coalfield
4 Paparoa coal, Greymouth Coalfield.

Table 3.2 Summary of mineral matter occurrence in West Coast coals

MINERAL	RELATIVE ABUNDANCE Paparoa coals	Brunner coals	NOTES (below)	TEXT DESCRIPTION (this work)
Silicates				
Quartz	●	●	1	3.1
Kaolinite	●	●	2	3.2
Illite	◑	◑	3	3.3
Chlorite	+	+	3	3.3
Carbonates				
Siderite	●	⊕	4	3.4
Calcite	+	⊕		3.5
Dolomite	+	⊕	5,6	3.6
Aragonite		○		3.5
Dawsonite		○	7	3.12
Sulphides				
Pyrite	+	◑⊕	8	3.7
Marcasite		+		3.7
Others				
Rutile	○	+		3.8
Crandallite	○	+		3.9
Apatite		+		3.10
Boehmite	+	○		3.11

Symbols

● Abundant
◑ Common
○ Minor
+ Trace
⊕ Locally abundant

Notes:

(1) Highly variable in abundance in Brunner coals; very abundant at Pike River but rare or absent in some plies at Greymouth and Buller.

(2) Present in all coals except rare Brunner plies.

(3) May include expandable interlayers.

(4) Brunner occurrence restricted to Flat Creek (Murchison).

(5) Abundant in Pike River Brunner coal only.

(6) Includes some ferroan dolomite (ankerite).

(7) Identified at Greymouth only.

(8) Strong vertical and lateral variations in Brunner seams.

3.2 QUARTZ

Quartz is extremely common and widespread throughout West Coast coals, although it does not consistently dominate the mineral assemblages. Samples where quartz is sparse or absent are usually restricted to highly kaolinitic coals which received only the finest detrital sediment, or plies where advanced silica leaching is inferred. Conversely, sample 37/016 (Paparoa Coal Measures) was found to contain abundant, fine grained quartz in the low density float fractions. This quartz, which also appeared in the -2μm fraction of the LTA, may be of authigenic origin.

In almost every occurrence, petrographic evidence shows quartz to be detrital in origin (Fig. 3.1), although a few examples of authigenic quartz are known from subbituminous and marginally bituminous Brunner coals. At Charleston, a Brunner seam contains a discrete band of euhedral quartz crystals, whereas the other occurrences comprise cherty horizons in the coal.

3.3 KAOLINITE

Kaollnite is commonly the dominant mineral in both Paparoa and Brunner coals, but is locally exceeded in abundance by concentrations of quartz, and by both quartz and illite in high ash coals. Rarely, kaolinite occurs subordinate to boehmite.

XRD patterns and SEM photographs indicate that kaolinite from the coals is well crystallised (Figures 2.5, 3.2, 3.3, 3.5, 3.10). Petrographic and SEM observations reveal widespread occurrence of kaolinite infilling cells and fungal spores (Figures 3.2, 3.3) , suggesting early authigenic formation prior to the collapse of open tissue structures. Lesser amounts of authigenic kaolinite can be seen in cleats and fractures, but it is not possible to estimate what proportion of total kaolinite is authigenic.

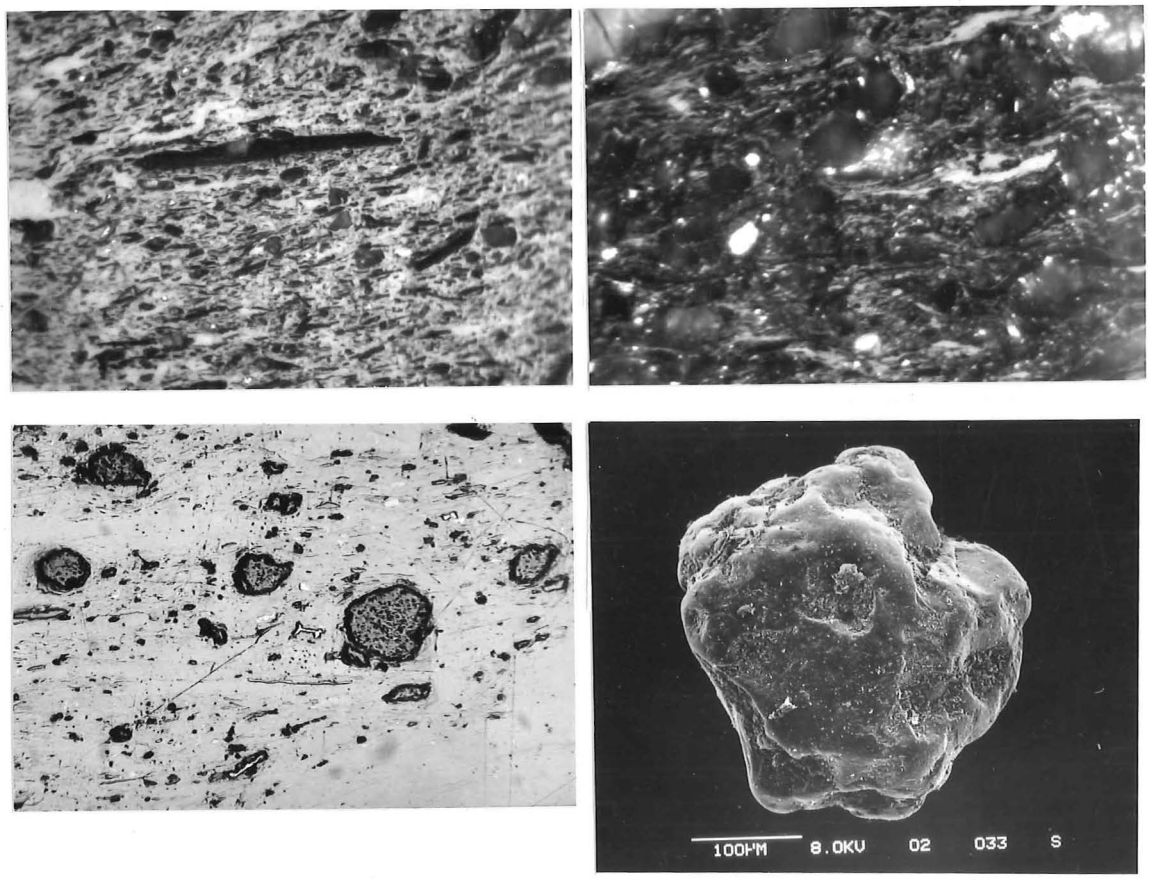


Figure 3.1 Detrital mineral matter.

Unless stated otherwise, all photographs are taken using reflected light and oil immersion.

(a) and (b) 'High-ash' coal from Brunner rider seam, Pike River Coalfield. The elongate grains (a) are predominantly muscovite/illite, and the subrounded, clear grains (b) are quartz. Both x250.

(c) Detrital assemblage of macerals (vitrodetrinite, minor inertodetrinite) and quartz grains. Sub-Morgan seam, Liverpool Mine (Morgan Member, Greymouth Coalfield). Air, x100

(d) Quartz sand grain from Paparoa coal, Strongman Mine (Rewanui Member, Greymouth Coalfield). SEM photo of LTA residues.

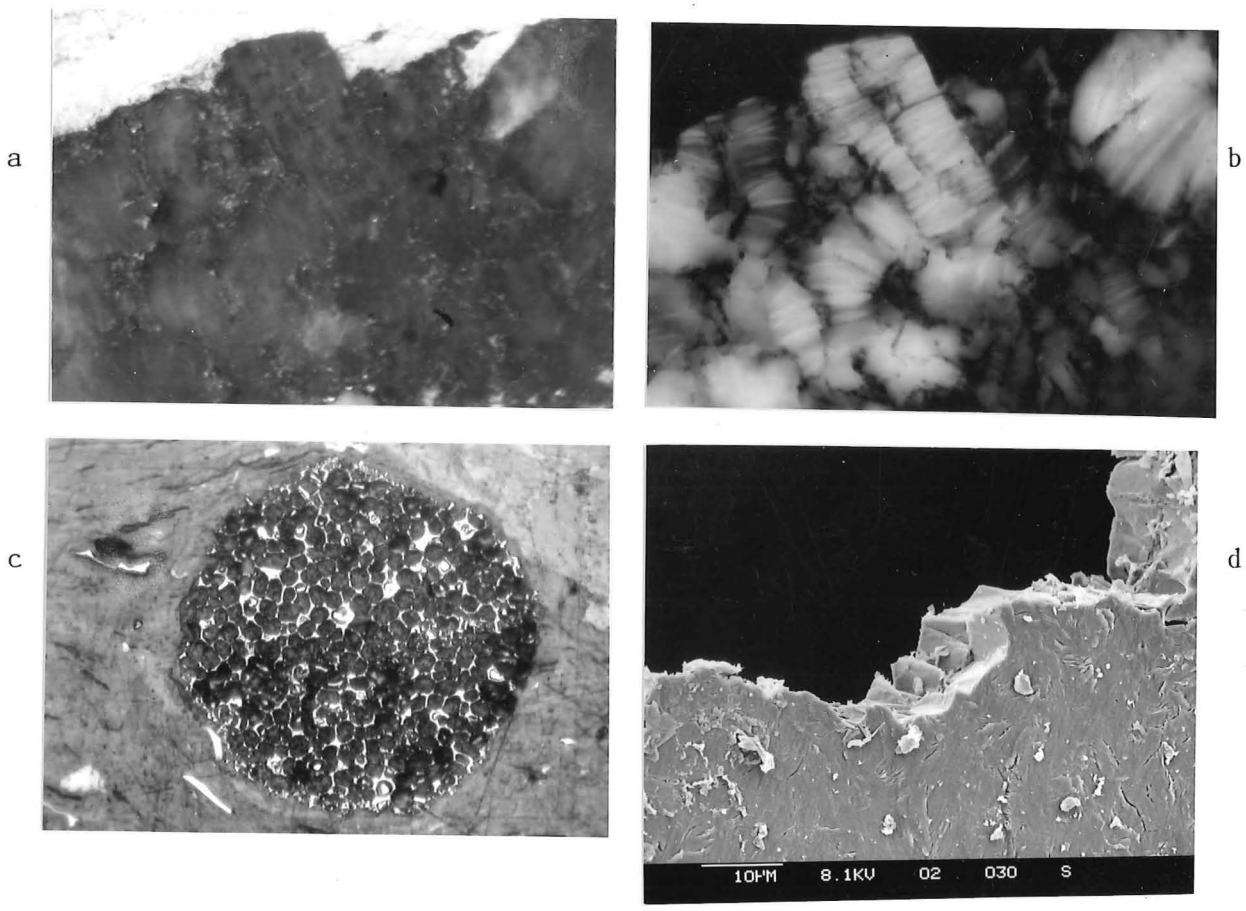


Figure 3.2 Authigenic kaolinite.

(a) 'Tonstein' kaolinite, formed by alteration of tuffaceous material. Specimen of Paparoa coal from Member 3 of Pike River Coalfield. x250, ordinary light.

(b) Same field as (a), photographed in fluorescence mode. The vermicular structure is revealed by fluorescing hydrocarbons which have impregnated the clays. x250, fluorescence.

(c) Kaolinite infilling fusinite in Paparoa coal from the Dunollie Member, Greymouth Coalfield. x 250

(d) Kaolinite occurring as a microcleat infilling. SEM photo of LTA residue.

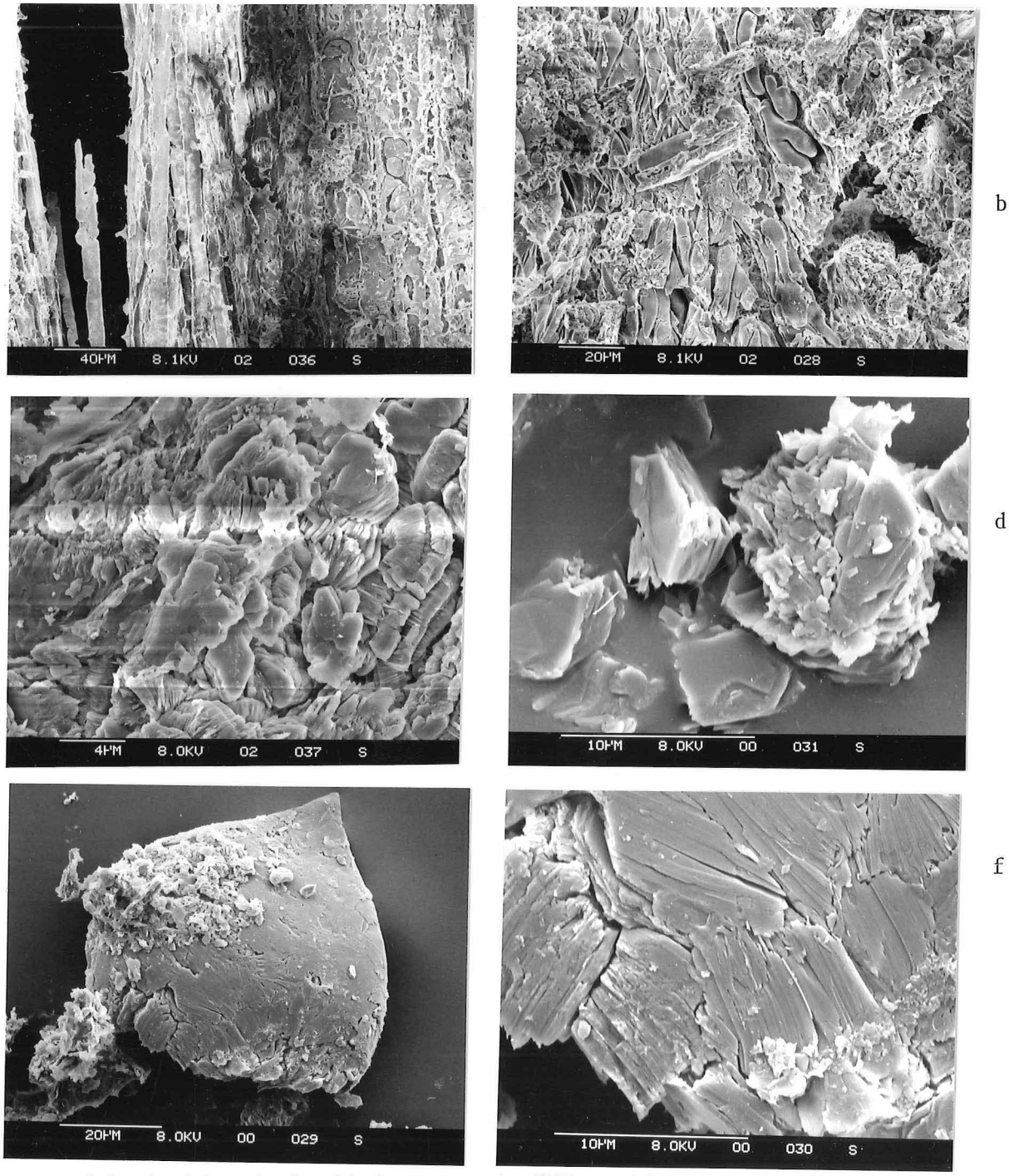


Figure 3.3 Authigenic kaolinite seen in SEM residues.

(a) Kaolinite 'casts' formed by infilling of tubular structure in plant tissue.
(b) Structures similar to those in (a), but less regular, possibly as a result of tissue collapse and compaction.
(c) and (d) Well crystallised kaolinite, showing vermicular and 'book' structure.
(e) Authigenic infilling, possibly from a seed or megaspore.
(f) Detail of lower edge, showing crystalline structure.

Samples (a) to (d) from Paparoa coal, Strongman Mine (Greymouth Coalfield).
Samples (e) & (f) Brunner coal, Mt William Mine (Buller Coalfield).

3.4 ILLITE, CHLORITE, AND EXPANDABLE CLAYS

The term illite will be used for the degraded muscovite/ hydrous mica group of minerals, and because of the preparation methods employed, this definition must be extended to include unaltered muscovite, regardless of grainsize. Expandable clay refers to the presence of swelling interlayers in illite or chlorite.

Illite is widespread in West Coast coal, but usually represents only a minor component in low ash samples. Otherwise, illite abundance is extremely variable. However, it is surprising that Soong and Gluskoter (1977) classify illite in their West Coast samples as "rare" (Table 3.1).

Chlorite is usually absent from the mineral assemblage, but appears in a few unusual Paparoa coals and is most common in low-ash Brunner coals, particularly those from parts of the Buller Coalfield. "Trace amounts" of chlorite were noted by Soong and Gluskoter (1977), but they did not indicate which samples this referred to. The occurrence of chlorite in low ash coal is difficult to explain, unless a diagenetic origin is envisaged (Chapter 8).

A variety of XRD peak morphology for clay mineral basal spacings is shown in Figures 3.4 and 3.5. Many of the coals appear to contain a proportion of substantially unaltered muscovite, as shown by fine mica flakes visible in LTA residues and polished section (e.g., Figure 3.1a). This is also indicated by the sharpness of some 10Å peaks, and the occasional prominence of well-defined peaks at 5Å.

The sloping "tail" region on the low angle side of illite 10Å peaks can be extended by the presence of small (thin) crystallites, internal disorder, and true interlayering (Brindley and Brown, 1980). Specimens with a large 10Å tail or unusual peak shape were tested for swelling by glycolation - heating sequences. Most of these showed little or no detectable expandability, maintaining their 10Å peak size and shape after glycolation and heating to 300°. Where expandability was observed, a general absence of distinct peaks in the 10-14Å region shows the interlayering to be dominantly random.

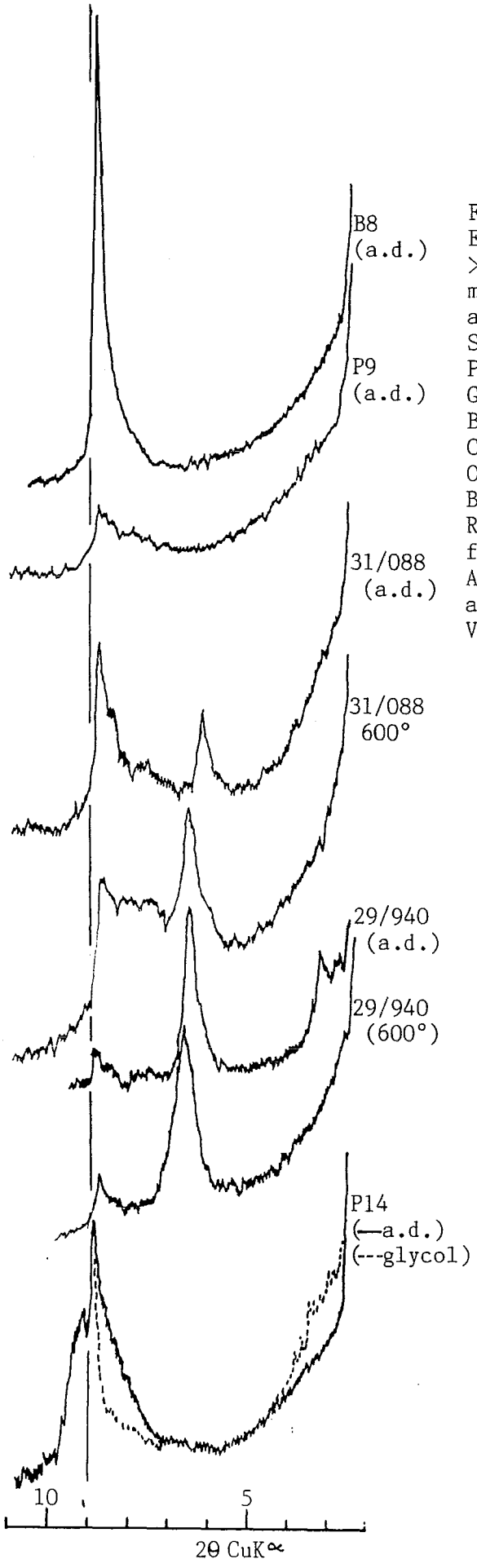


Figure 3.4
Examples of XRD traces over the >8Å interval for mineral matter from various Paparoa and Brunner coals.
Samples:
P9,P14 Paparoa coals from Greymouth Coalfield.
B8 Brunner coal from Greymouth Coalfield.
Others are Brunner coals from Buller Coalfield.
Refer to Tables in Chapters 4 & 7 for other details.
All traces from oriented mounts.
a.d. = air dried
Vertical line show at 9° 2θ.

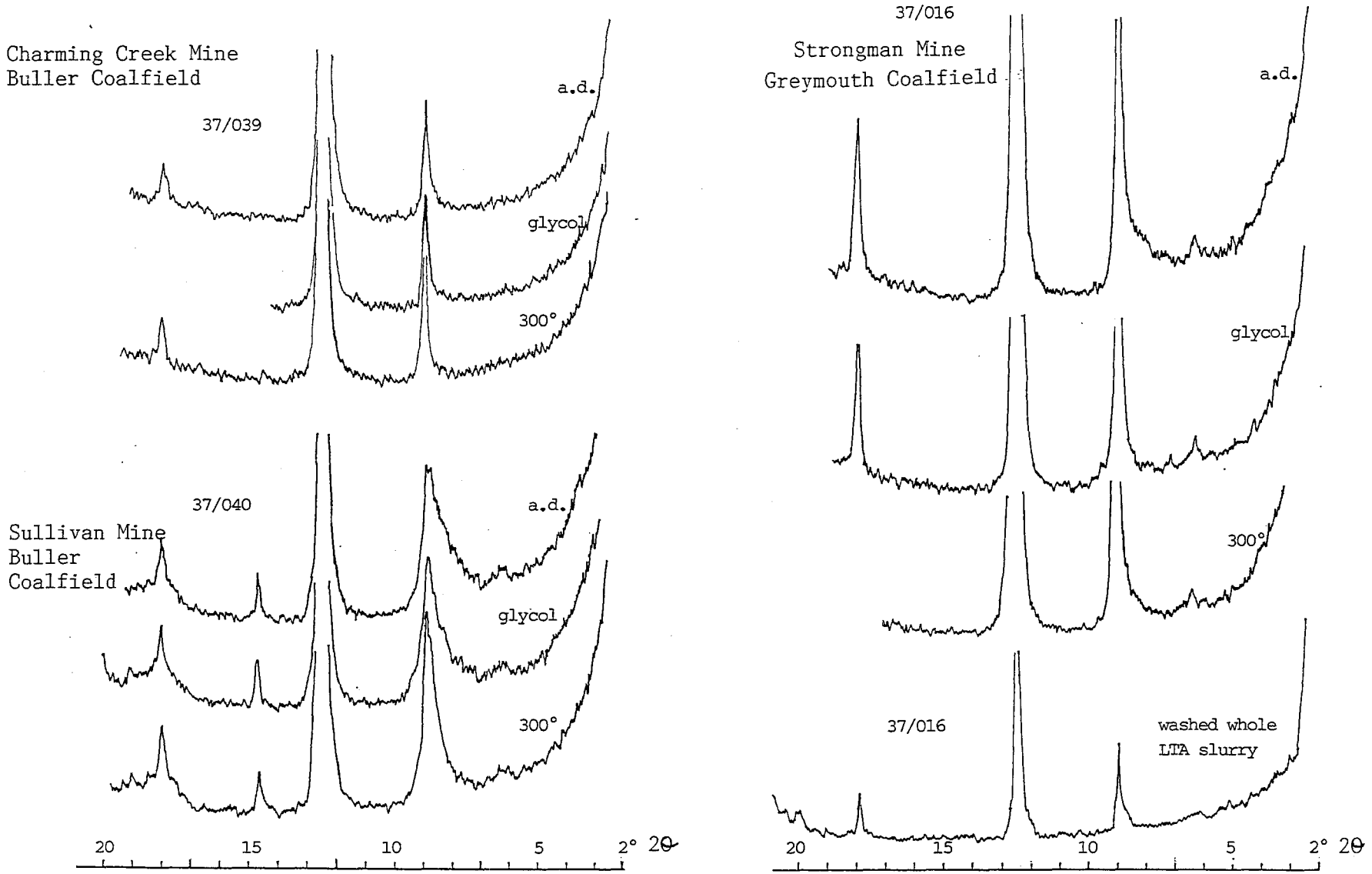


Figure 3.5 XRD traces for sedimented mounts of clay fraction, separated from LTA and dispersed by citrate-dithionate treatment. For comparison, trace at lower right is for smear mount of washed, whole LTA.
a.d. = air dried; glycol = ethylene glycol saturated; 300° = heated at 300°C for 1 hour.

Mineral matter from three run-of-mine coals was processed to extract and prepare a well-dispersed clay fraction, in accordance with the method of Ward (1977). XRD patterns for these fractions (Figure 3.5) confirm the paucity of expandable clay, and the sharpness of some 10Å peaks, in the -2μm fraction.

Broad 10Å illite peaks commonly showed little change on heating to 300°C, suggesting that these illites contained "intergrade" hydroxy interlayers (Jackson, 1963), which prevent complete collapse on heating, and may result in an increase in 10Å disorder for heated samples (Rich, 1968). For some samples, these characteristics were seen to persist after acetic acid/citrate-dithionate treatment, which tends to dissolve hydroxy interlayers (Rich, 1968). The persistence of a disordered 10-12Å peak after heating to 600°C, for sample 31/088 (Figure 3.4), is interpreted as indicative of irregular interlayering between illite, smectite, and chlorite.

Part of the Mössbauer spectrum for a Paparoa coal (26/030 + 26/032) has been assigned to biotite by Pankhurst et al., (1986). This could not be confirmed by XRD, but may indicate the presence of a minor trioctahedral component in the illite. Because biotite is rapidly degraded in peat environments, it is rarely found in coal. However, the drillcore log indicates that these samples may incorporate sheared sediment and "chuckie stones" (drop stones), either of which may be a source of biotite. A low ash Brunner coal gave an entirely dioctahedral illite response when examined by the Mössbauer technique.

3.5 SIDERITE

Siderite is very abundant in Paparoa coals at Greymouth, where it occurs as small blades, spherules, or elongate nodules, a few mm in thickness (Figure 3.6c). However, it occasionally forms larger concretions, and occasionally massive veinlet networks in bands up to 10 cm thick and several metres long , parallel to bedding, known to the miners as "brass" or "brass stone".

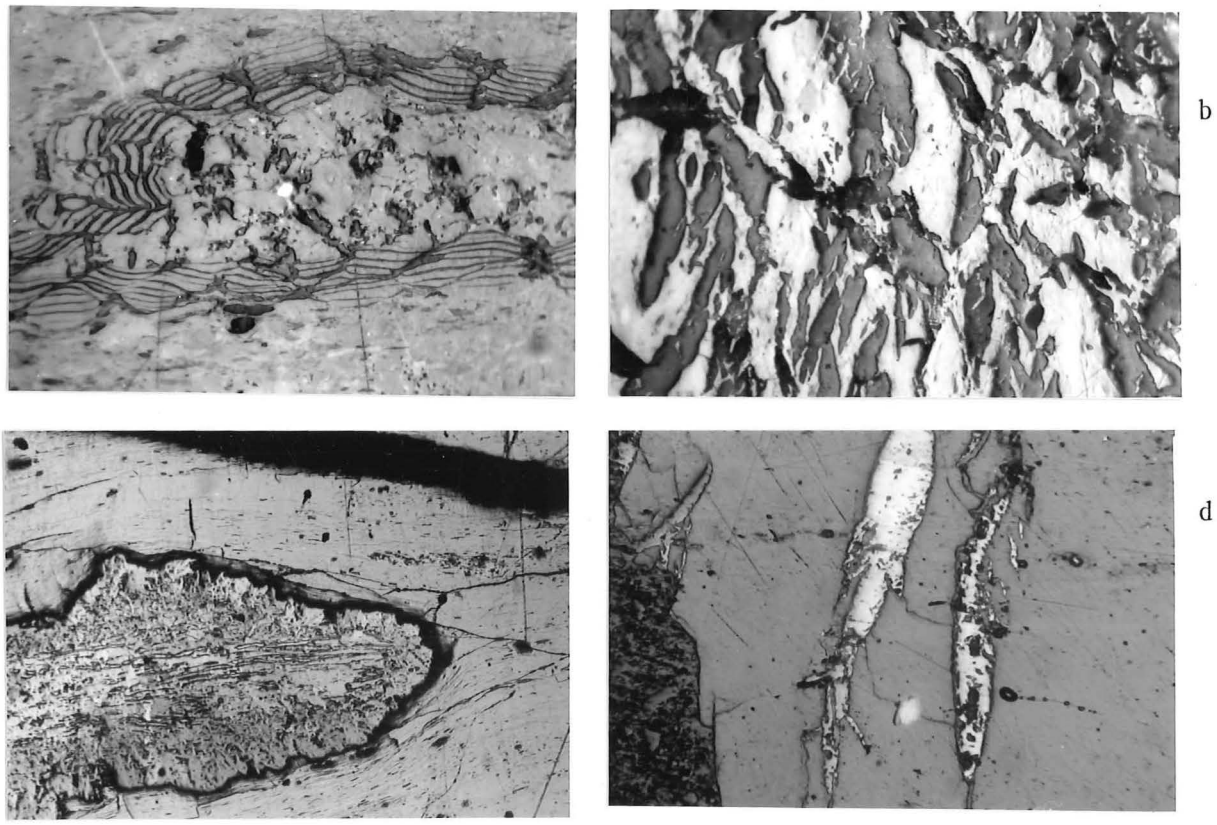


Figure 3.6 Carbonate minerals.

(a) Localisation of dolomite within stem structure. Main Brunner seam, Pike River Coalfield. x250
(b) Anastomosing network of dolomitic veinlets in sheared coal. Main Brunner seam, Pike River Coalfield. x250
(c) Siderite microconcretion, Paparoa coal. Specimen from Liverpool Mine (Morgan Member, Greymouth Coalfield) shows a typical occurrence of siderite. Uncompressed fusinite remnants within the mineral show evidence of early replacement origin. x25, air
(d) Fracture located siderite in coal from the Tiller Mine (Dunollie Member, Greymouth Coalfield). x100

Authigenic siderite is also common throughout the interseam sediments of the Paparoa Coal Measures, forming concretions in the mudstones and replacing ferromagnesian minerals, especially biotite, in the coarser lithologies. Compaction features around siderite nodules in coal show this mineral to be of early diagenetic origin.

Sparse siderite occurs in dolomitic nodules within Brunner coal seams at Garvey Creek, but is otherwise restricted to seams of the Paparoa coal measures.

3.6 CALCITE AND ARAGONITE

Paparoa coals contain sparse veinlets of calcite, which occur in association with large masses of siderite. XRD data for these veinlets show compositional variation from low- to high-magnesium calcite, suggesting different generations of late diagenetic formation.

In Brunner coals, calcite is generally a widespread but minor epigenetic mineral, except in the case of the Pike River Coalfield, where the Brunner seam contains abundant calcite and dolomite (Figure 3.6a, b). Whereas most of the carbonate in this seam occurs in small, irregular fractures, some occurs in concretionary masses or shows preferential location within maceral structures (Figure 3.6a), and may have a diagenetic origin.

One sample of Brunner coal from Greymouth (sample B20) contains aragonite, which accompanies calcite and dolomite. Carbonate veining seen in hand specimen suggests that all three minerals occur epigenetically in the coal.

3.7 DOLOMITE AND ANKERITE

The term dolomite strictly refers to the mineral $Ca(Mg,Fe,Mn)(CO_3)_2$ in which there is less than 20 mol.% substitution of magnesium by iron; the more iron-rich species are termed ankerites. Both dolomite and ankerite occur sporadically in the Paparoa coals, but are principally restricted to sideritic "brass" bands and nodules, and may originate by

alteration of siderite. Abundant, low-iron dolomite accompanies calcite in Brunner coal at Pike River (Figure 3.6a,b), and occasionally occurs as veins in Reefton Brunner coal. However, small (2-4 mm) spherulitic nodules found in Brunner coal at the Flat Creek Coalfield consist of ankerite.

3.8 PYRITE AND MARCASITE

Both pyrite and marcasite are found in almost all West Coast coals. Marcasite is comparatively rare, and only occurs accompanying pyrite (Figure 3.7a, 3.8e).

The gross distribution pattern of pyrite in West Coast coals is relatively simple. In Paparoa coals, pyrite is usually present in trace amounts, visible in petrographic mounts, but not sufficiently abundant to show in XRD traces of whole mineral matter. Exceptional abundances appear where the coal has been locally mineralised along fractures or shear zones, or where siderite has altered to sulphide (Figure 3.7).

In Brunner coals, pyrite is more common (Figure 3.8), except in weathered samples where the sulphide may be replaced by iron oxide pseudomorphs, or simply by voids (Figure 3.9). In some unweathered Brunner plies, pyrite can form more than 80% of the total mineral matter, particularly where detrital minerals are sparse.

Well formed framboidal pyrite is uncommon in West Coast coals, and a variety of irregular shapes may represent overgrown framboids. Preferential replacement of clays by pyrite in sediment horizons within or near Brunner seams is common and, in extreme examples from sediment immediately overlying coal, the entire clay matrix and some quartz grain material has been replaced (Figure 3.8f).

The absence of sulphides in the data of Soong and Gluskoter (1977) is anomalous (Table 3.1), and probably results from use of old, oxidised samples as discussed in 3.14.

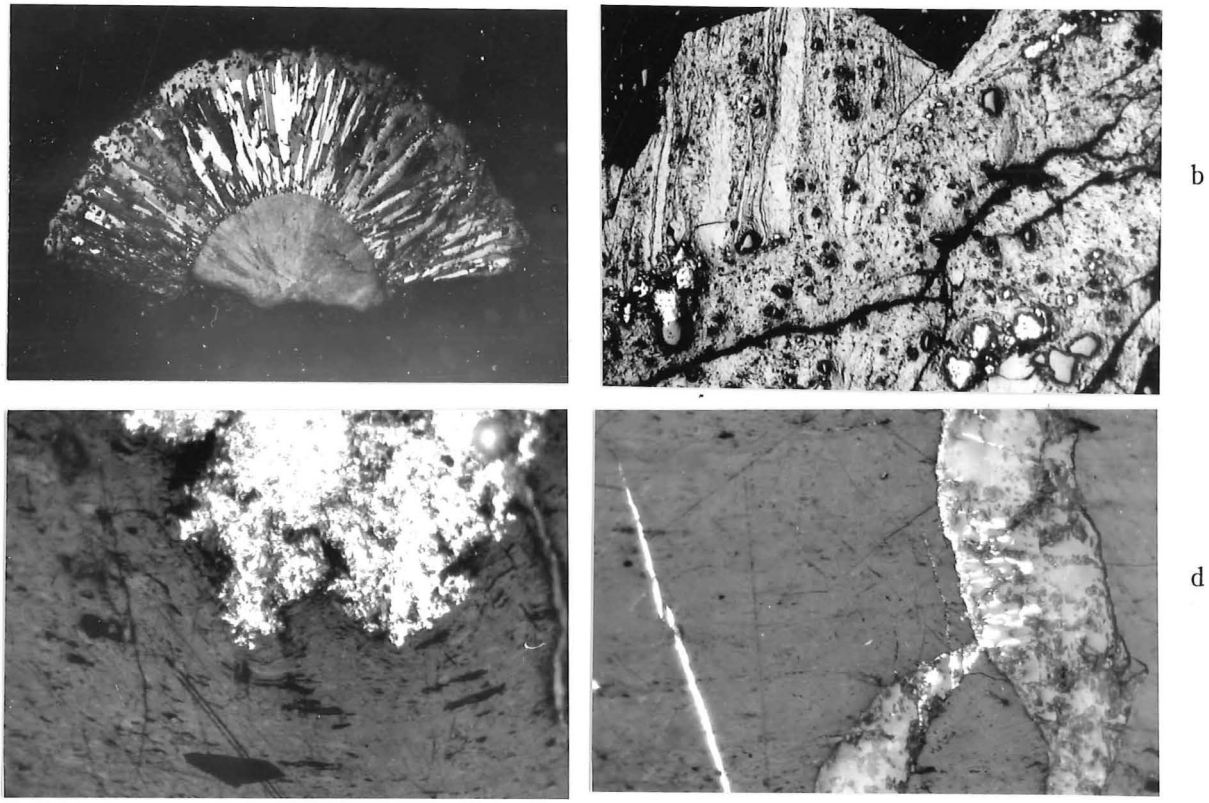


Figure 3.7 Sulphides replacing carbonate in Paparoa coals.

(a) Fragment of a marcasite nodule formed by replacement of siderite in coal from the Rewanui Member, Paparoa Coal Measures, Greymouth (sample 26/657, Drillhole 633). Core and rim zones are pyritic, suggesting multi-stage development. x25, crossed filters.

(b) Sheared coal from the sample in (a), showing a healed fracture zone, containing fragmented carbonate and pyrite. x25

(c) Pyrite pseudomorphing nodular siderite in coal from the Tiller Mine, Dunollie Member, Greymouth. x250

(d) Pyrite replacing siderite in Tiller Mine coal, sample as for (c). x250

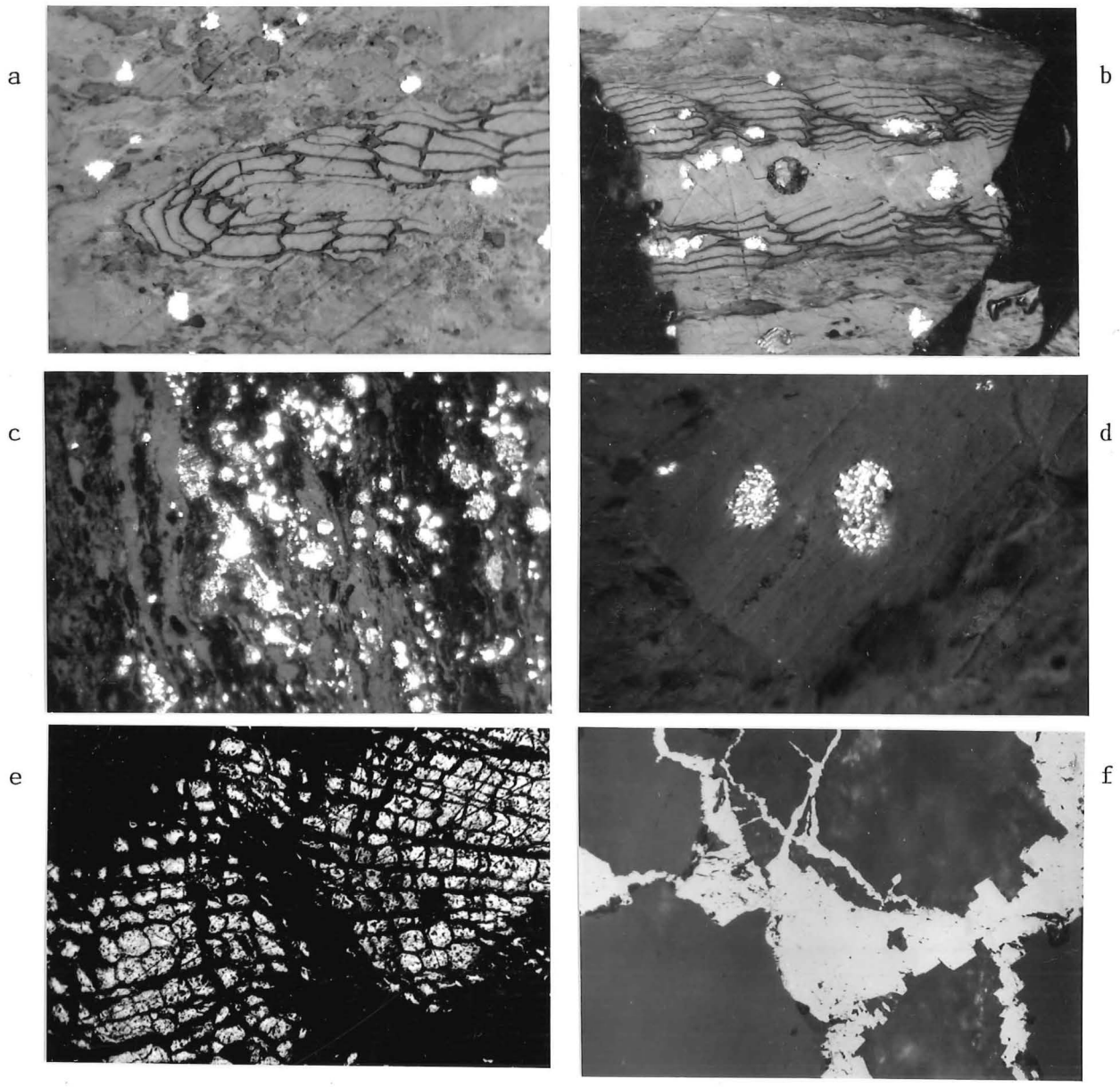


Figure 3.8 Pyrite in Brunner coal and associated sediment.

(a) and (b) 'Suberinite' macerals and irregular crystalline pyrite in main Brunner seam, Pike River Coalfield. x250
(c) High ash coal containing abundant pyrite, with some areas of well formed framboids, Thin rider seam, Pike River Coalfield. x250
(d) Detail of framboids in (c). x625
(e) Infilling of cells, or replacement of cell contents, by pyrite. Main Brunner seam, Pike River Coalfield. x100
(f) Concretionary pyrite replacing clay matrix and granular quartz in sandstone roof of upper Brunner seam, Island Block Opencast, Garvey Creek. x100, air

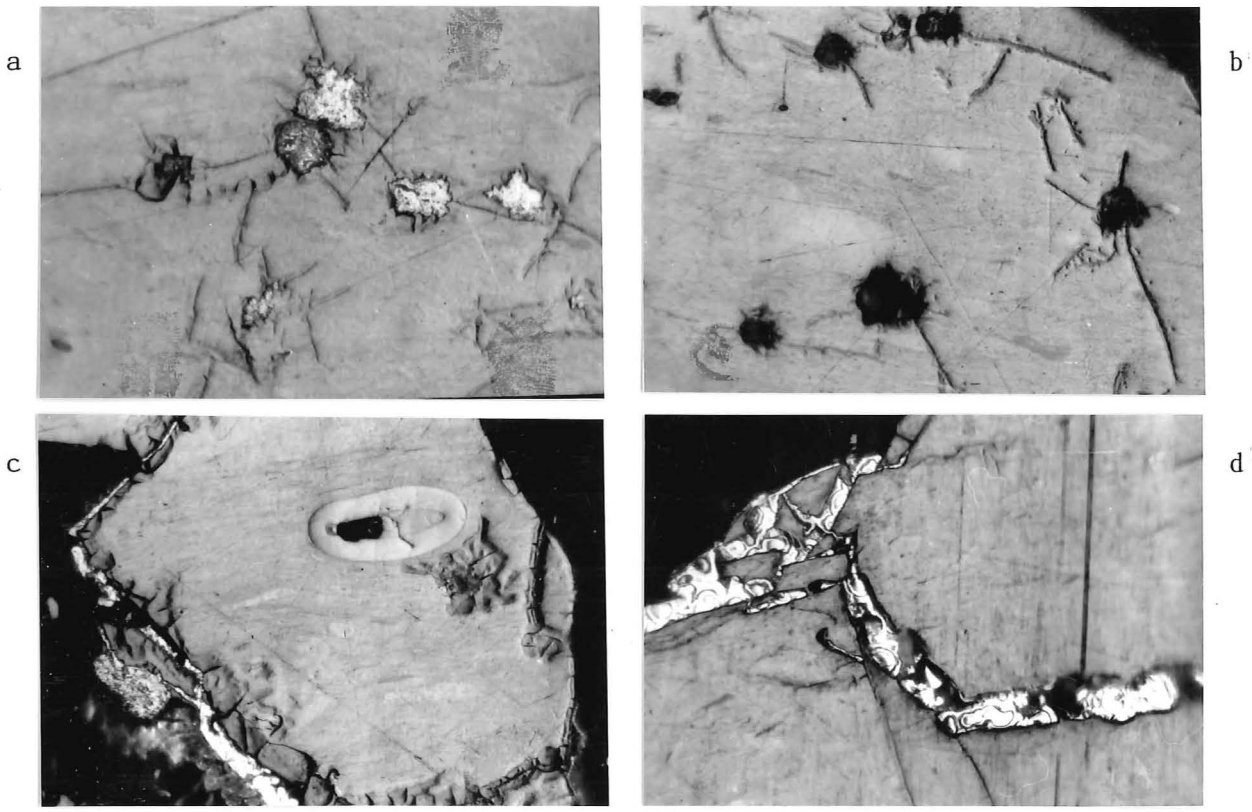


Figure 3.9 Effects of weathering seen in the top composite from Drillhole 1241, Webb/Baynes area, Buller Coalfield. A11 x250

(a) Iron oxide pseudomorphs after pyrite.
(b) Complete dissolution of pyrite, leaving cavities.
(c) Hematite, probably pseudomorphing pyrite veinlets, and oxidation cracks radiating from fractures.
(d) Concentric zonation of hematite which grew from solution in open fractures.

3.9 RUTILE

Rutile is a common but minor mineral in both Paparoa and Brunner coals. Although the XRD peaks are usually very weak, good confirmation of this mineral is provided by a correlation of distinct 3.25Å peaks and high-titanium ash compositions (Figure 3.10). Although no titanium mineral was identified petrographically, mineral matter from a titanium-rich coal showed fibres of probable TiO_2 composition when examined by SEM-microanalyser (Figure 3.11). The origin of these fibres is unknown.

3.10 CRANDALLITE

Phosphorus-rich mineral matter yielded XRD peaks which can be assigned to the mineral crandallite, an aluminophosphate of general formula $CaAl_3(PO_4)_2(OH)_5H_2O$ in which calcium is commonly substituted to some extent by barium, strontium, transition metals, and rare earths (Figure 3.10). Very similar minerals, probably isostructural with calcian crandallite, have been described from coal in New South Wales (Ward, 1978) and U.S.A. (Finkelman et al., 1979; Finkelman, 1980).

A definitive classification of these minerals is still unavailable, and it is not possible to determine composition from XRD data alone. Ward identified aluminophosphate minerals in strontium-rich coal, and therefore preferred the name goyazite group, based on the strontian end-member $SrAl_3P_2O_7(OH)_7$, to describe the occurrence. Similarly, other authors adopt the term plumbogummite group, based on aluminophosphate occurrences in metalliferous deposits. The classification adopted in this work follows the usage in the JCPDS Mineral Powder Diffraction File (Data Book, 1980) i.e., crandallite sensu strictu, goyazite, and the barium equivalent, gorceixite, are all considered members of a crandallite group (Table 3.3).

No phosphorus minerals have been identified in West Coast coal petrographically, although small (1 μm) phosphorus-bearing nodules were detected in mineral matter by SEM (Figure 3.11). Crandallite is assumed to occur in the coals as a finely dispersed residual mineral produced by weathering during peat accumulation; precursor materials may be detrital

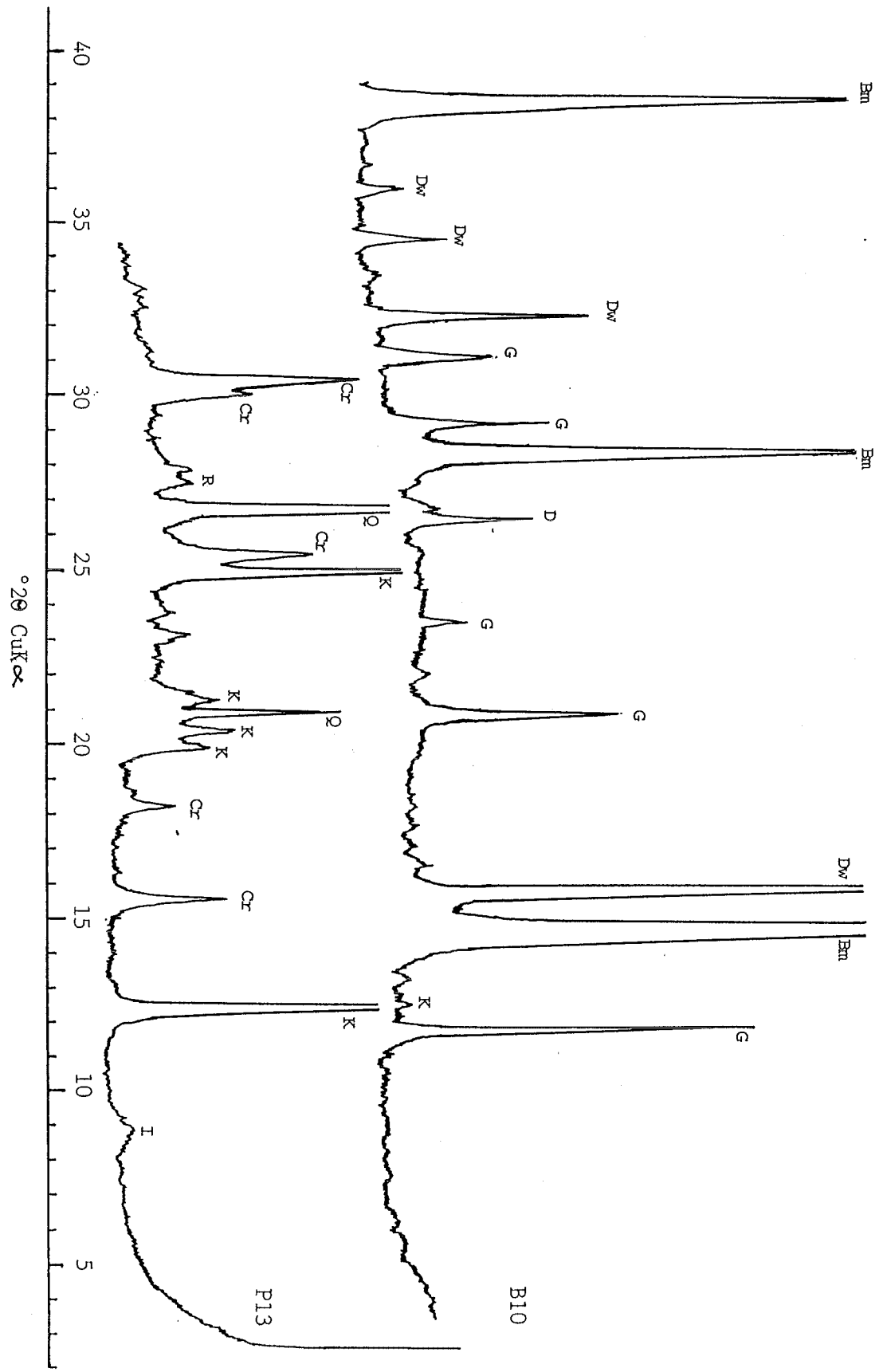
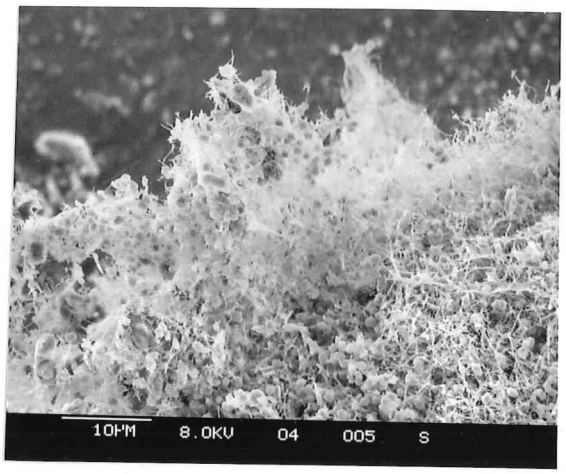
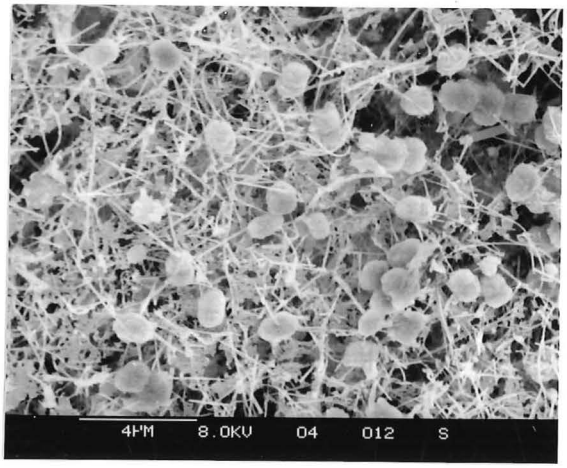


Figure 3.10 XRD traces for smear mounts of whole LTA. Top: LTA containing Boehmite and Dawsonite (Greymouth Brunner coal). Bottom: LTA containing Crandallite and Rutile (Greymouth Paparoa coal).
Symbols: G gypsum K kaolinite I illite Q quartz Dw dawsonite Bm boehmite Cr crandallite R rutile

a



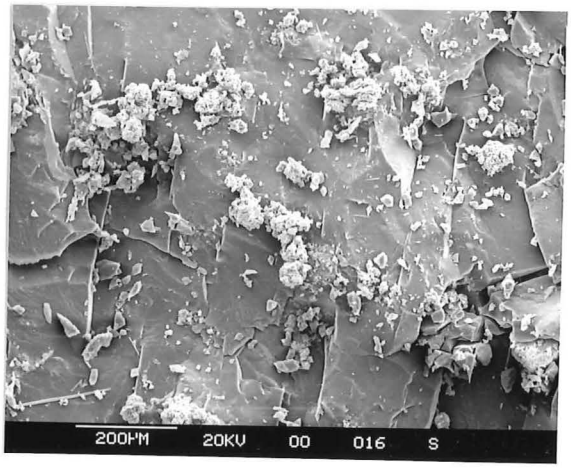


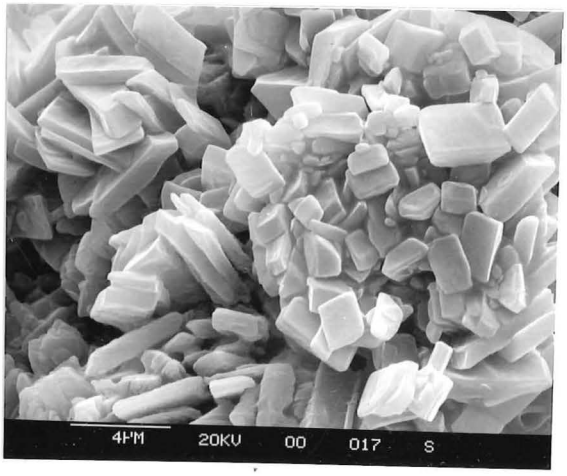
b

Figure 3.11 (a) SEM photo of LTA residues from Paparoa coal containing abundant crandallite and rutile. The fibres have a high-Ti composition, and are assumed to be rutile, whereas the nodular structures contain both titanium and phosphorous, and are assumed to represent crandallite with TiO_2 coatings. Sample P13 (Table 4.1).

(b) Detail of (a).

a





b

Figure 3.12 (a) SEM photo showing sulphate efflorescence on laboratory stored Brunner coal (Buller Coalfield).
(b) Detail of efflorescence encrustation.

16-162* *triclinic*			25-119* *hexagonal*			25-1457* *hexagonal*			Observed in West Coast coals (this work).
dÅ	I	*hkl*	dÅ	I	*hkl*	dÅ	I	*hkl*	dÅ	order of (decreasing) intensity
5.75	35	$10\bar{1}$	5.70	80	101	5.70	34	101	5.70	3
			4.85	70	021	4.87	29	021	4.87	5
3.53	35	$02\bar{2}$	3.51	75	110	3.51	35	101	3.51	2
3.42	6	200								
3.40	8	$12\bar{1}$								
3.08	6	$1\bar{3}1$								
2.97	100	$\bar{1}31$	2.98	70	021	2.983	50	021	2.99)¶	4
2.88	10	$21\bar{1}$	2.93	100	113	2.941	100	113	2.94)¶	1
2.73	14	$1\bar{3}2$	2.85	10	015	2.858	6	015		
			2.70	20	006	2.699	17	024		

* File No., JCPDS Mineral Powder Diffraction File *Data Book 1980*
¶ commonly unresolved

Table 3.3 XRD data for crandallite in West Coast coals.

apatite, and soil-bound or vegetal phosphorus.

3.11 APATITE

Only two examples of apatite in West Coast coal are known, both from Brunner coals. Apatite in a Garvey Creek coal was accompanied by abundant crandallite, and may represent partial weathering of detrital apatite. The other occurrence, from Buller Coalfield, yields very weak and poorly defined XRD peaks. Poorly crystalline apatite of authigenic origin is inferred.

3.12 BOEHMITE

West Coast coal samples with very high-alumina ash composition have been known for many years, attracting little comment and no interpretation (Gage, 1952; Hughson, 1953; Bowden and Roberts, 1975). More recently, Gray (1981) has drawn attention to some Buller Coalfield samples exhibiting a distinctly hyperaluminous ash composition, i.e. containing more alumina than can be accounted for by the presence of kaolinite.

The alumina-rich coals at Buller Coalfield, and even more extreme

examples from Brunner coals at Greymouth, all contain the mineral boehmite (γ-AlO[OH]). This mineral is the chief source of "surplus" aluminium in the coals, although crandallite and dawsonite (3.13) also contribute to a minor extent.

The presence of boehmite is attributed to persistent leaching of aluminosilicate minerals in the peat swamps during Brunner time, leading to a net loss of silica. Although rare examples of boehmite in Paparoa coal are also known, development of this mineral, together with other important mineralogical trends, is considered to be characteristic of stable, well drained, and long-lived Brunner peat swamps.

Very few occurrences of boehmite or other aluminium oxide/hydroxide minerals in coal have been reported. "Bauxite" was described from Indian coal by Mitra (1954), but no specific minerals are identified. Bouska (1981) classed boehmite as a very rare mineral, but provided no further details. Diaspore has been recorded as a trace mineral from a number of North American coals by Finkelman (1980), and Mackowsky (1982) listed diaspore (α-AlO[OH]) as a rare mineral, citing an occurrence in a kaolin-coal tonstein of probable volcanic origin. Adolphi and Storr (1985) list both diaspore and boehmite in low temperature ash, presumably from German coal.

The identification of "bauxite" by Mitra (1954) must be regarded as doubtful. The relevant d-spacings quoted do not match any known lateritic mineral, and may represent a mixture of minerals. It is notable that the corresponding ash composition had a ratio Al_2O_3/SiO_2 = 0.54, which was regarded by the author as "aluminium rich", although this ratio is low in comparison to that of the hyperaluminous West Coast ashes.

Boehmite can be produced from gibbsite ($Al[OH]_3$) at temperatures in the range 140° - 200°C, although the conversion is very slow (Deer et al., 1962) . The possibility of this transition occurring in the oxidation process was tested by processing a sample by the peroxide method (Ward, 1974) at 70°C. the result confirmed boehmite as the only aluminohydroxide mineral present.

3.13 DAWSONITE

The rare aluminocarbonate mineral dawsonite ($NaAlCO_3[OH]_2$) is commonly found as a minor mineral component in Greymouth Brunner coals, where it accompanies boehmite in hyperaluminous samples (Figure 3.10, Table 3.4). Until the mid-1960's dawsonite was known from only seven localities in the world, but has subsequently been described from a number of zeolitic assemblages including extensive deposits in the Green River Formation of Colorado (Smith and Milton, 1966).

Occurrences in the coal and coal measures of the Sydney basin have been reported by Loughnan and See (1967), and Loughnan and Goldberry, (1972). The description of dawsonite in Australian coals indicates an epigenetic occurrence as cleat, joint, and fracture infillings, but the original site, time and conditions of formation are unknown. The Greymouth examples show no relationship to epigenetic formation, and are assumed to represent finely dispersed material within the coal, of diagenetic origin.

To eliminate the possibility that dawsonite in LTA might represent an oxidation artifact, occurrence of this mineral in whole coal was confirmed by XRD (Figure 3.10).

19-1175¶ *orthorhombic*			Observed, Greymouth Brunner coal (this work)	
dÅ	I	*hkl*	dÅ	I*
5.67	100	110	5.65	vs
3.38	60	200	3.39	
3.31	20	121		
3.09	20	130		
2.784	90	211	2.78	s
2.601	70	040	2.60	
2.500	40	112	2.50	
2.221	30	231	2.22	w
2.151	60	202	2.15	w
2.066	20	240,132		
1.988	70	150	1.99	

¶ File No., JCPDS Mineral Powder Diffraction File *Data Book 1980*
* Observed intensity from slurry film mount. Intensities also influenced by preferred orientation.
vs = very strong s = strong w = weak

Table 3.4 XRD data for dawsonite in Greymouth Brunner coals.

3.14 GYPSUM

Although gypsum occurs sporadically throughout West Coast coals, all occurrences can be attributed to surface weathering, deep circulation of meteoric water in fracture zones, or atmospheric alteration of exposed or stored coal (Figure 3.12a). All crushed or ground coal samples will eventually develop a gypsum component if both sulphide material and available calcium are present. Furthermore, it is well known that low rank (subbituminous and lignite) coals, which may contain significant anounts of organically bound calcium, commonly produce calcium sulphates during LTA oxidation (Given and Yarzab, 1978; Miller et al., 1979; Adolphi and Storr, 1985).

For these reasons, it is considered misleading to record gypsum as a component of mineral assemblages, except in restricted circumstances, e.g., where mineral matter corrections are required for individual samples. Soong and Gluskoter (1977) concluded that New Zealand coals contain large amounts of sulphate minerals in comparison to overseas coals, but this must be considered incorrect. Their data (Table 3.1, this work) are deficient in pyrite due to the use of aged coal samples, and possibly also due to unsuitable oxidation techniques (see Appendix 1). Their report of anhydrite in the West Coast samples can be attributed to dehydration of gypsum by overheating.

The relatively good drainage and high rainfall which characterise most West Coast coalfields has been effective in removing gypsum and other sulphates soon after their formation. In many areas where abundant calcite and sulphides coexist (e.g. the Pike River Brunner seam), gypsum may be unexpectedly absent due to outcrop leaching. It is notable that because gypsum is common in stored specimens, it is often wrongly expected to occur in fresh samples. Many of the West Coast drill logs and subsequent reports (e.g., Bowman, 1982) contain frequent misidentification of kaolinite or carbonate minerals as gypsum.

3.15 OTHER MINERALS ATTRIBUTED TO RECENT OXIDATION

In outcrop coals, several recent oxidation minerals other than gypsum occur (Table 3.5), all as a result of iron sulphide decomposition. Isolation and XRD of sulphate hydrates is extremely difficult, and much of the iron oxide-hydroxide material is too poorly crystalline to show an identifiable XRD pattern. Mössbauer spectroscopy of whole coal, however, provides a useful method of detecting these minerals, although a poor detection limit restricts the technique to iron-rich samples. The Mössbauer results (Pankhurst et al., 1986) also confirm the presence of other iron minerals identified by XRD (e.g. siderite, pyrite, chlorite).

As for gypsum, the iron-bearing oxidation minerals have been excluded from the assemblages in the tables, although records of the occurrence of recent weathering minerals have been retained. These data together with petrographic evidence of weathering (oxidation cracks and voids, see Figure 3.9) can explain an anomalous absence of sulphides and carbonates, and indicate a potential loss of whole-coal sulphur. Various iron sulphate minerals found in coarsely crushed coal after approximately one year's storage are shown in SEM photographs (Figure 3.12). It should be noted that even drillcore samples are commonly affected by in-situ weathering in parts of Buller Coalfield where coal occurs in near-surface, highly jointed rocks.

Table 3.5 Recent weathering minerals commonly identified in coals.

*Szomolnokite	$FeSO_4.H_2O$
Rosenite	$FeSO_4.4H_2O$
Melanterite	$FeSO_4.7H_2O$
*Coquimbite	$Fe_2(SO_4)_3.9H_2O$
*"Ferrous sulphate"	?
*Goethite	α - FeOOH

*Identified in West Coast coal by Mössbauer spectroscopy (Pankhurst et al. 1986).

CHAPTER 4

SAMPLE LOCATION AND MINERALOGICAL ANALYSES

4.1 SAMPLE LOCATION AND ORGANIC CHARACTER

Sample locations are shown in Figures 4.2–4.8, which also show other localities mentioned in the text, and where possible, basic coalfield geology and rank contours or trends. In the case of the Brunner Coal Measures, only the main seam is worked at each locality. For the more stratigraphically complex Paparoa Coal Measures, which at Greymouth contain worked seams at several horizons, a column is provided which shows the stratigraphic relationships of the major mines (Figure 4.3).

Determination and expression of rank for New Zealand coals is discussed in detail by Suggate (1959), Newman and Newman (1982, 1983), Suggate and Lowery (1982), and Newman (1985a, 1985b). Vitrinite reflectance, volatile matter, and specific energy are all unsatisfactory parameters if used alone, probably due primarily to major variations in vitrinite character (Newman, 1985b). The rank classification scheme of Suggate (1959), based on both volatile matter and specific energy, has been used for rank contours shown on the coalfield maps which appear in this chapter. The derivation of "rank numbers" used by Suggate's scheme, and their approximate relationship to vitrinite reflectance is shown in Figure 4.1. Table 4.1 provides representative proximate analyses, Specific Energy and sulphur (all on an air dried basis), swelling number, and where possible, maceral composition and vitrinite reflectance.

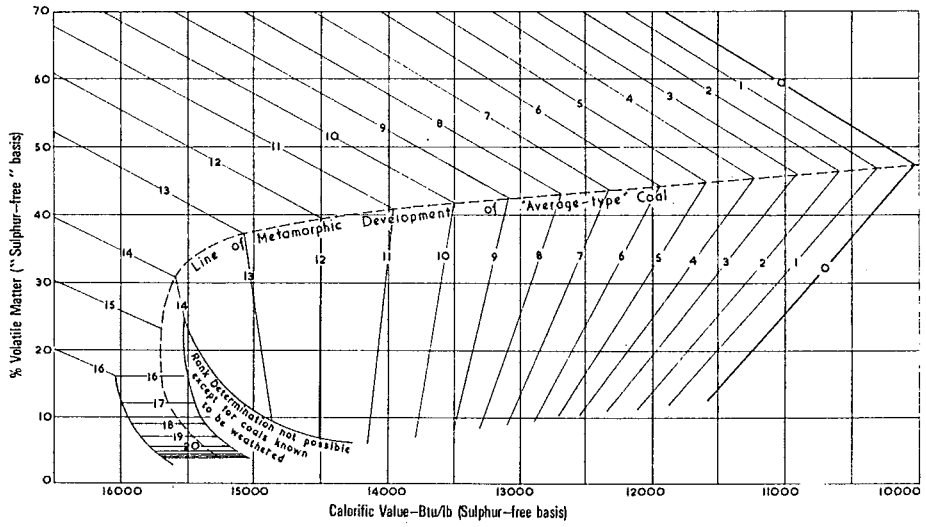


Figure 4.1 (a, above) Derivation of "Suggate Rank numbers" from volatile matter and Specific Energy.
(b, below) Relationship between Suggate Rank and vitrinite reflectance.
Both figures from Suggate & Lowery (1982).

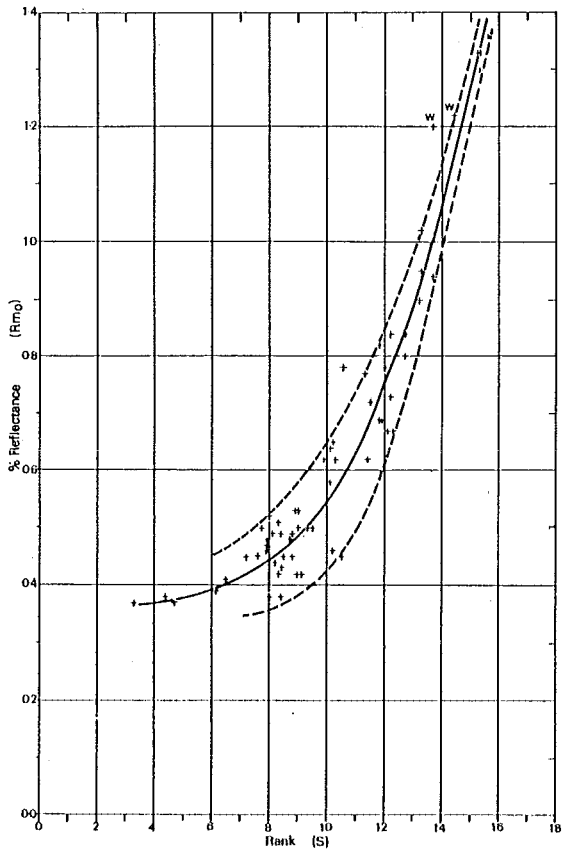


Table 4.1

Representative proximate and petrological analyses for West Coast coals from the area of study. Proximate analyses expressed on an air-dried basis.

Sample location	Sample type	CRA No	Date	Moist	Ash	VM	FC	S	Specific Energy MJ/Kg	Specific Energy Btu/lb	CSN	Macerals V,E,I mmf	Ro	Coal Meas.
Greymouth Coalfield														
Liverpool Mine	ROM	21/712	1978	1.0	5.5	34.6	58.9	.24	34.00	14617	9+	90, 8, 2	.94^	P, Morgan
Strongman Mine	ROM	21/703	1978	6.5	4.6	36.9	52.0	.28	29.98	12889	1.5	87, 9, 4	.69^	P, Rewan.
Drillhole 628 (11m)	core	26/376	1981	9.9	3.2	37.2	49.7	.29	29.14	12528	1	82, 5,13	.54¶	P, Rewan.
Curries Mine #	-	CS403	1941	6.1	3.4	39.7	50.8	.80	29.80	12810	3	n.a.	n.a.	P, Dunol.
Dobson Mine	face	CS905	1946	.7	5.8	43.2	50.3	1.70	33.03	14200	8	n.a.	n.a.	Brunner
Wallsend Mine	face	CS900	1946	.5	6.5	41.8	51.2	2.20	32.87	14130	8.5	n.a.	n.a.	Brunner
Birchfield Opencast	face	21/708	1978	8.8	4.0	38.1	49.1	1.06	27.65	11887	1	82,18, 1	.62^	Brunner
Pike River Coalfield														
PR75 (2m)	OC	27/531	1981	.8	6.9	37.0	55.3	.36	33.99	14610	9+	91, 3, 6	.83*	P, M4
Drillhole 6 (7m ply)	core	33/045	83/84	1.2	5.1	41.7	52.0	.64	33.97	14600	9+	82,13, 5	.70*	Brunner
Buller Coalfield														
DH 1220 (11m ply) (Webb/Baynes Block)	core	31/069	1983	1.2	.2	32.0	66.6	1.40	35.87	15420	9+	95, 1, 4	1.04*	Brunner
Sullivan Mine	ROM	21/725	1978	.8	6.6	27.0	65.6	3.18	33.05	14209	8.5	96, 1, 3	?1.30^	Brunner
DH 1277 (2.7m ply) (Upp. Waimangaroa)	core	35/328	1985	3.8	.7	41.8	53.7	2.92	32.67	14040	5.5	94, 4, 2	.65*	Brunner
Charming Creek Mine	ROM	21/723	1978	2.3	3.4	41.0	53.3	5.71	31.78	13663	6.5	94, 4, 2	?.76^	Brunner
Reefton/Garvey Ck Coalfields														
Island Block Mine	ROM	21/718	1978	3.2	2.6	40.4	53.8	2.09	31.40	13500	3	88,11, 1	?.78^	Brunner
"	ROM	30/344	1982	3.8	3.4	39.6	53.2	1.34	30.49	13108	2	n.a.	n.a.	Brunner
Burkes Creek Mine (now Welcome)	ROM	21/715	1978	10.0	1.2	38.2	50.6	1.08	27.89	11990	1	90, 7, 3	.65^	Brunner
Waitahu Mine (old Dauntless)	ROM	37/033	1985	7.6	2.2	44.8	45.4	5.79	27.83	11965	.5	n.a.	n.a.	Brunner
Flat Creek Coalfield														
DH13 (1m ply)	core	50/293	1987	1.2	1.5	37.4	59.9	.34	34.70	14920	9+	n.a.	n.a.	Brunner
Inangahua Area														
Burleys Opencast	ROM	30/348	1982	18.4	3.3	37.4	40.9	3.32	22.09	9497	0	n.a.	n.a.	Brunner
Heaphy Opencast	ROM	21/722	1978	17.3	3.8	33.0	45.9	1.00	23.91	10279	0	94, 4, 2	.50^	Brunner
"	ROM	30/347	1982	17.0	4.0	34.8	44.2	1.46	23.55	10125	0	n.a.	n.a.	Brunner
Charleston Area														
McLaughlins Opencast	ROM	21/724	1978	20.5	3.8	36.2	39.5	4.96	21.75	9351	0	92, 4, 4	.45^	Brunner

NOTES: # near Tiller Mine ^ from Black (1980) ? value for different sample
* from Newman (1985a) ¶ from ACIRL analyses from similar location

OC = outcrop sample ROM = run of mine sample P = Paparoa Rewan. = Rewanui Member
Dunol. = Dunollie Member DH = Drillhole n.a. = not available

Ro = vitrinite reflectance in oil immersion, various bases, refer original sources.
Data, other than petrology, are from NZ Coal Research Association (or the Dominion Laboratory in the case of old analyses).

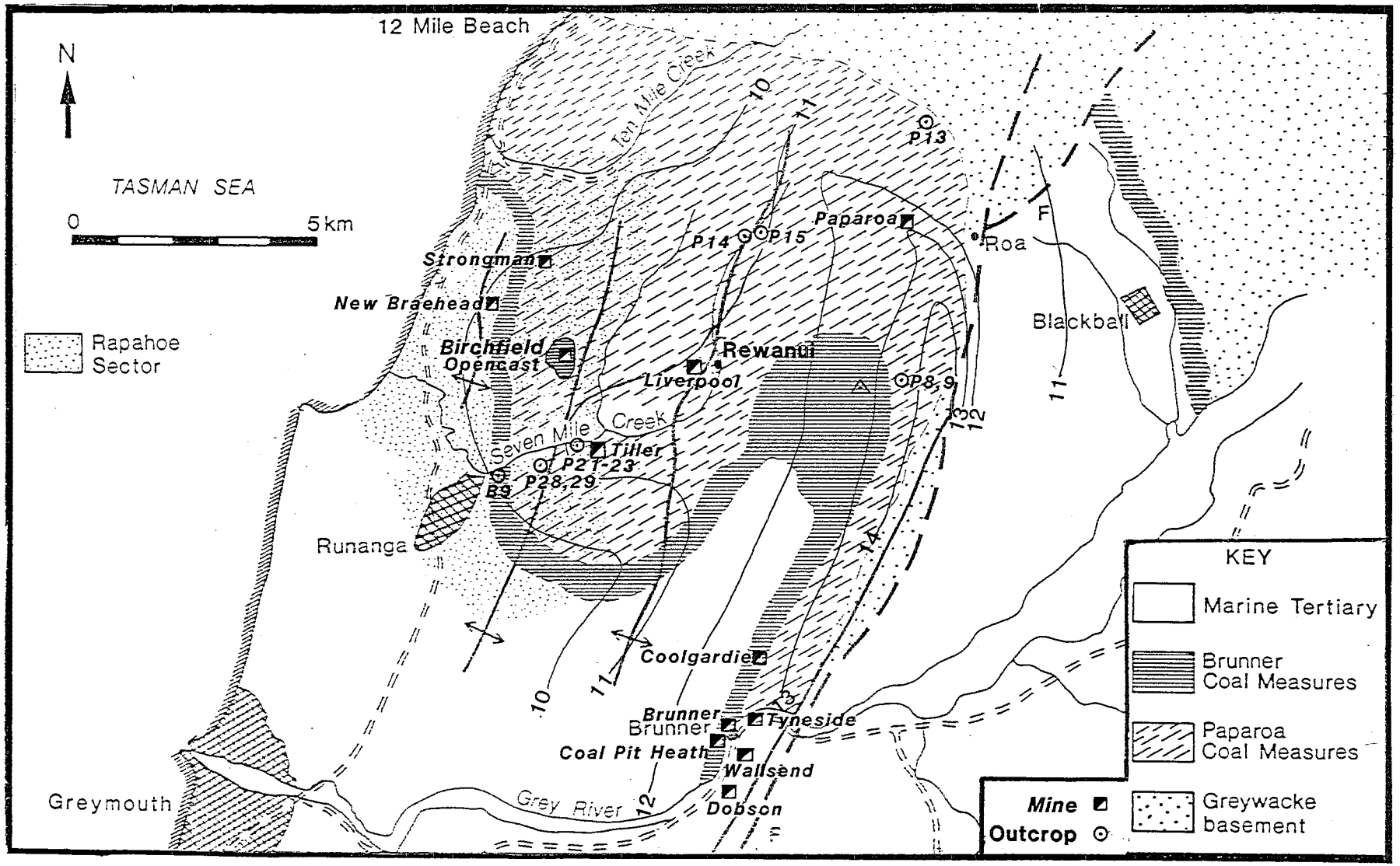


Figure 4.2 Map of Greymouth Coalfield showing sample locations and rank trends for the Brunner horizon. Adapted from Newman (1985a) and Suggate (1959).

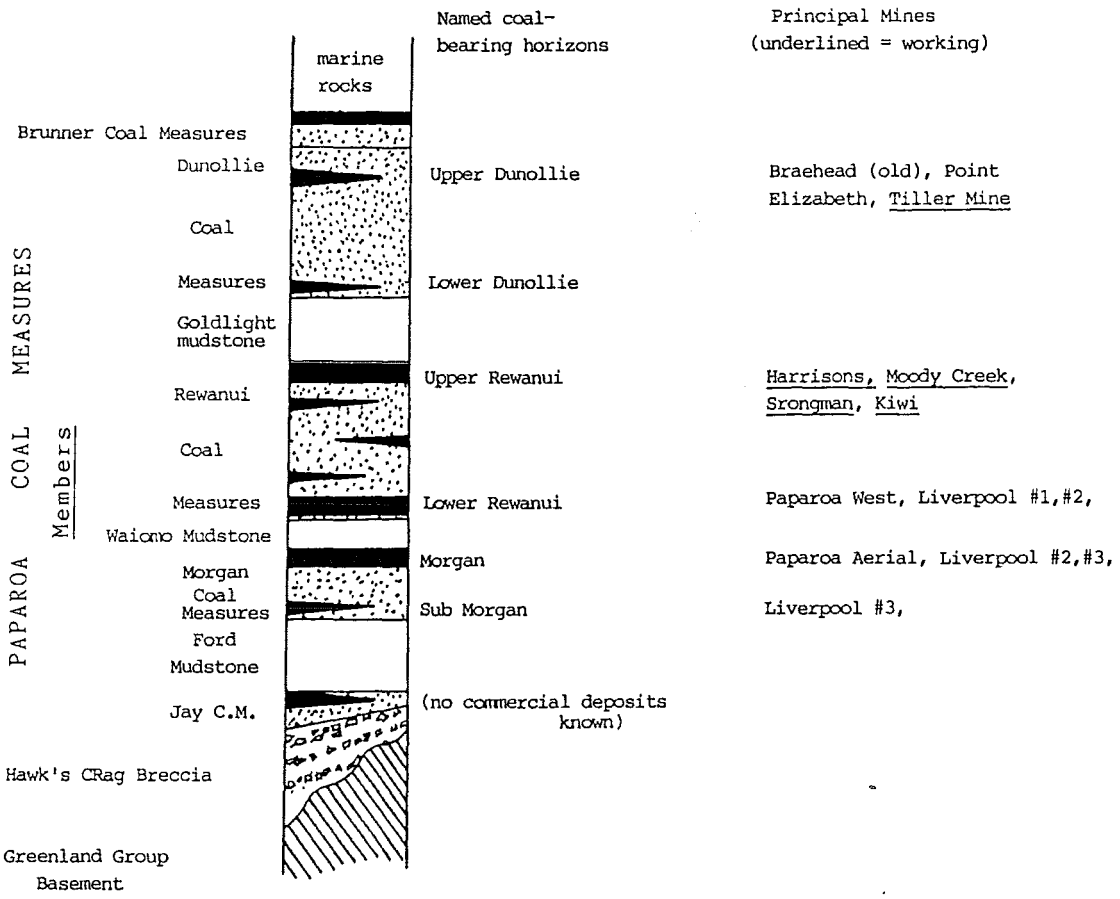


Figure 4.3 Paparoa coal-bearing horizons at Greymouth Coalfield, showing named seams and stratigraphic location of some mines. Adapted from Gage (1952).

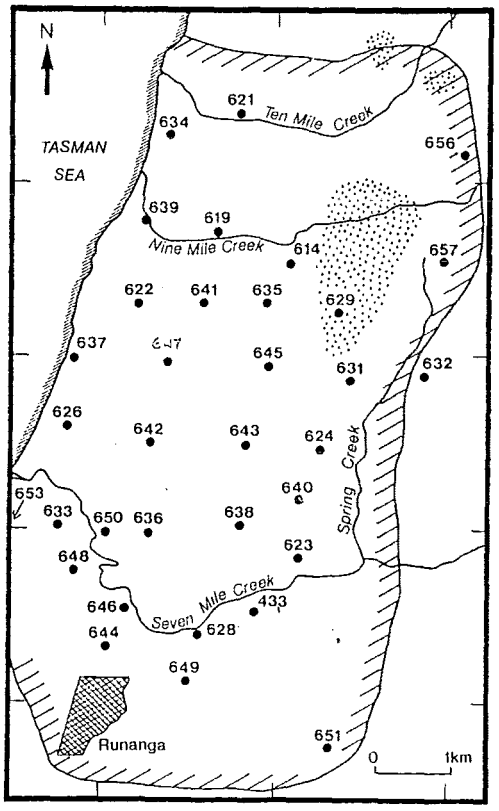
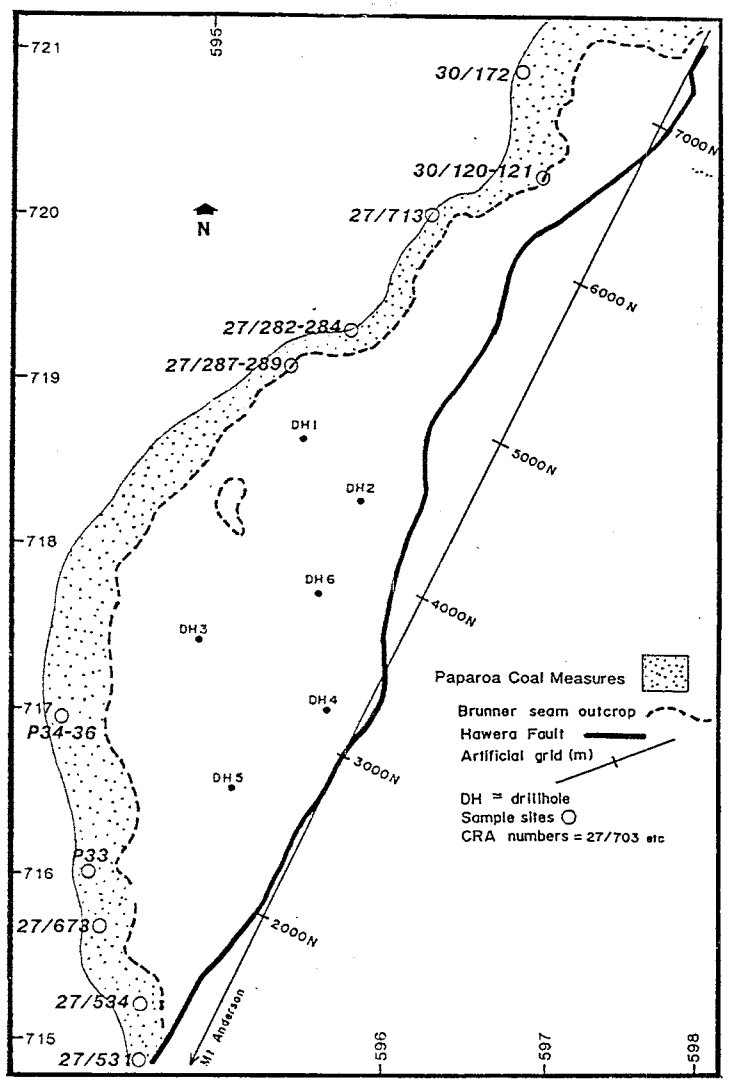


Figure 4.4 Detail of the Rapahoe Sector, Greymouth Coalfield, showing the location of drillholes mentioned in the text. Adapted from Newman (1987).



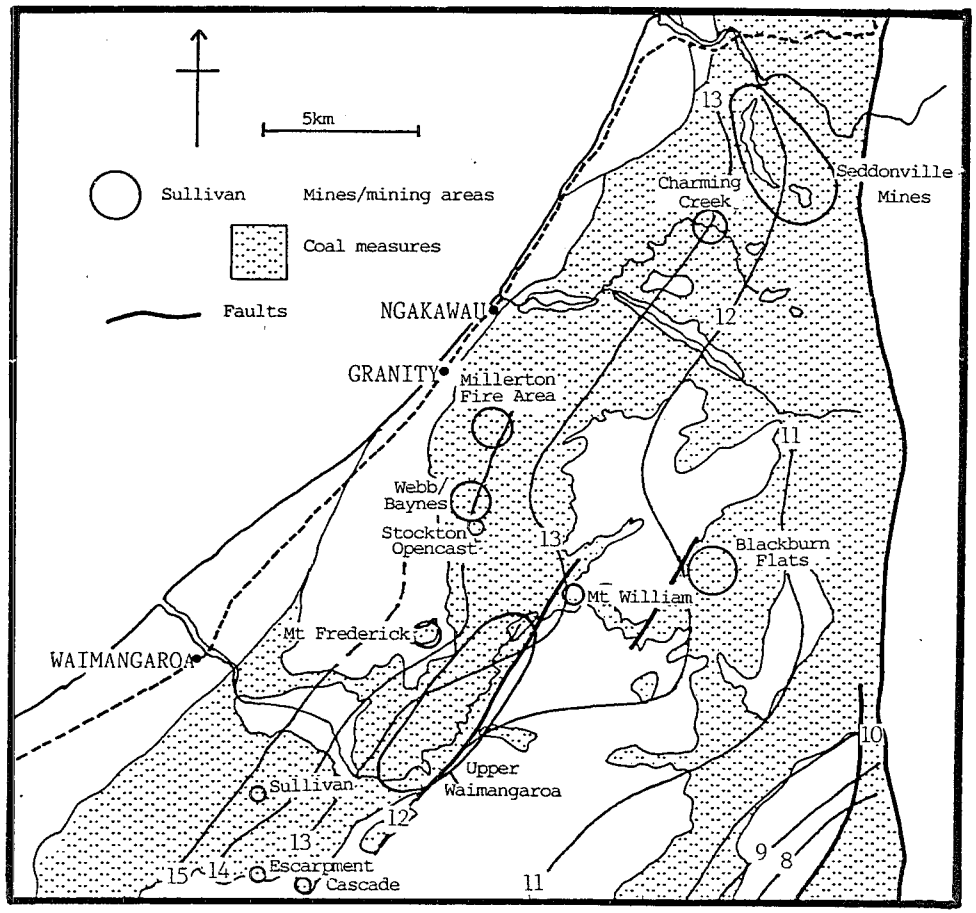
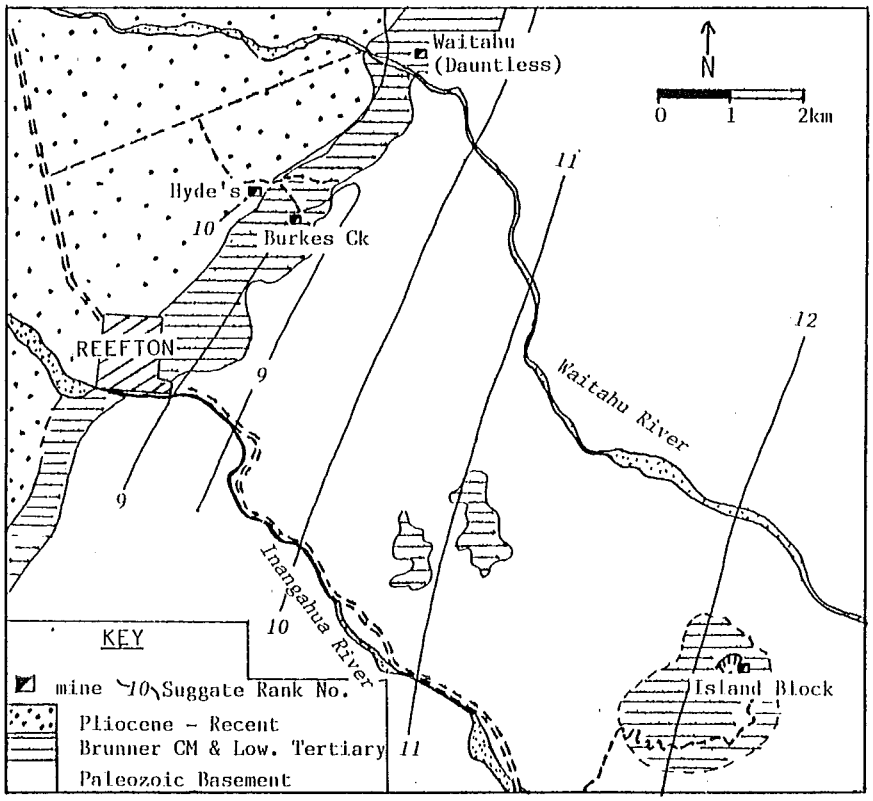


Figure 4.5 (left). Pike River Coalfield, showing Drillhole and outcrop locations of samples obtained from the Paparoa and Brunner Coal Measures. Coal rank is uniformly high volatile bituminous A. Adapted from Newman (1985a).

Figure 4.6 (above) Buller Coalfield, showing mining and exploration areas mentioned in the text. Numbered contour lines show Suggate Rank. Adapted from Willet (1965) and Suggate (1959).



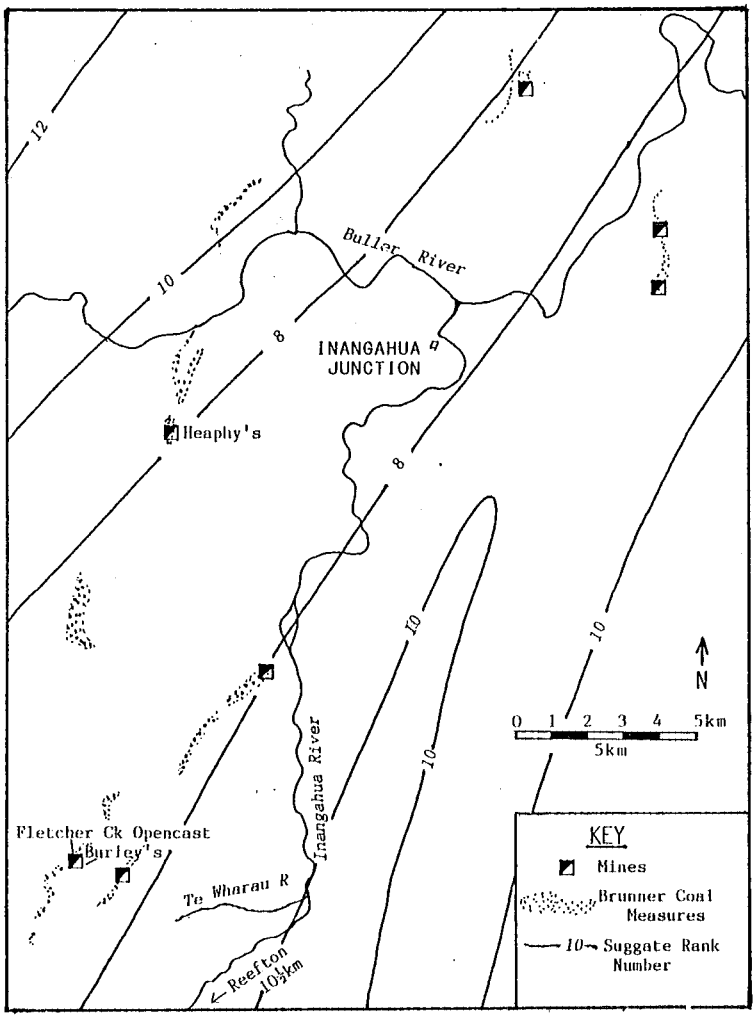


Figure 4.7 (above) Reefton and Garvey Creek Coalfields, showing locations referred to in the text. Adapted from Willet (1965) and Suggate (1959).

Figure 4.8 (left) Subbituminous coals mined in the Inangahua area. Adapted from Willet (1965) and Suggate (1959).

4.2 SAMPLE DESCRIPTION AND MINERALOGICAL ANALYSES

4.2.1 Samples examined as part of this project

All samples examined by the writer are included in Tables 4.2 and 4.3, where details of sample type (e.g., ply, full seam, run-of-mine) and mineralogical analysis (by XRD) are provided. Also listed are measurements of high temperature ash, and percentages of total quartz, kaolinite, and illite, expressed to base 100%, estimated from both XRD measurement and ash constituents analyses as outlined in Chapter 2.

Coal samples obtained from Coal Research Association of New Zealand (CRA) have been identified by their CRA number, which is always in the form XX/XXX. Other samples, collected by the writer, have been assigned a serial number which is prefixed by a "P" to denote Paparoa Coal Measures, or "B" to denote Brunner Coal Measures.

The data have been divided into separate groups, representing Paparoa coals (Table 4.2) and Brunner coals (Table 4.3) respectively. A small number of mudstones from the Paparoa Coal Measures were also analysed, and the results are presented separately in Chapter 6 (Tables 6.1 & 6.2). Further tables (Tables 4.4 & 4.5) list calculated, quantitative mineral composition for each of the samples for which an ash constituents analysis was available; the same division into separate tables for Paparoa coals, Brunner coals, and mudstone samples has been used. Ash constituents analyses for all samples, except the mudstones and other non-coal lithologies, and two Paparoa seam profiles described in Chapter 6, appear in Appendix 2.

4.2.2 Analytical data from other sources

A series of 14 ash constituents analyses were made available by Pike River Coal Company Ltd., and have been incorporated in the computed analyses appearing in Table 4.5. A further 337 ash constituents analyses for West Coast coals, carried out by CRA and Australian Coal Industry Research Laboratories (ACIRL) for the New Zealand Coal Resources Survey, were also made available. These analyses, all from drillcore samples, were made up as follows:

Rapahoe Sector, Greymouth Coalfield (Paparoa coals), 104 samples
Webb-Baynes Block, Buller Coalfield (Brunner coals), 118 samples
Upper Waimangaroa Sector, Buller Coalfield (" ") 115 samples

These data have been incorporated in graphs appearing in following chapters, and both computed mineral assemblages and the ash constituents analyses have been listed in Appendix 2.

4.3.3 A Comparison of Results from XRD and Calculation Methods.

Some of the mineral tables in this chapter permit a direct comparison of the results of the two methods of estimating mineral assemblages, with respect to quartz, kaolinite and illite (Figure 4.9). Although the overall correlation is fair, there is a high degree of scatter. Some of the more extreme deviation from the parity line can be attributed to unusual mineralogy, e.g., a high degree of interlayering in illite, the presence of aluminous phases such as dawsonite, or a large proportion of siderite. XRD values for kaolinite and illite are probably greatly affected by errors in determining quartz. For very low ash coals, it is difficult to prepare and adequately grind small LTA samples to a consistent grainsize. This problem appears to be worst for the samples prepared early in the project, when operator technique was more variable.

In the case of drillhole samples with CRA numbers, an additional source of error may be attributed to dissimilarity between splits of inadequately ground coal of the same sample distributed to analytical laboratories for ash constituents analysis, and to the writer for XRD analysis (see 2.2). This problem can be expected to be particularly severe where the seams contain "chuckie stones" (drop stones), which are common in many Paparoa coals of the Rapahoe Sector.

Overall, the calculation method is considered to offer the more reliable and least biased procedure for calculating mineral assemblages, although the limitations which have been discussed should be considered when interpreting results obtained by this method. Calculated quartz-kaolinite-illite data have therefore been adopted for comparing coals on variation diagrams appearing in Chapters 6 and 7, and calculated values

used for the more complete mineral assemblages listed in Tables 4.4 and 4.5, and Appendix 2.

It is stressed that the calculation method is based on observed mineralogy and mineral character determined by XRD and petrography, and without this input the method would revert to the status of arbitrary normative analysis.

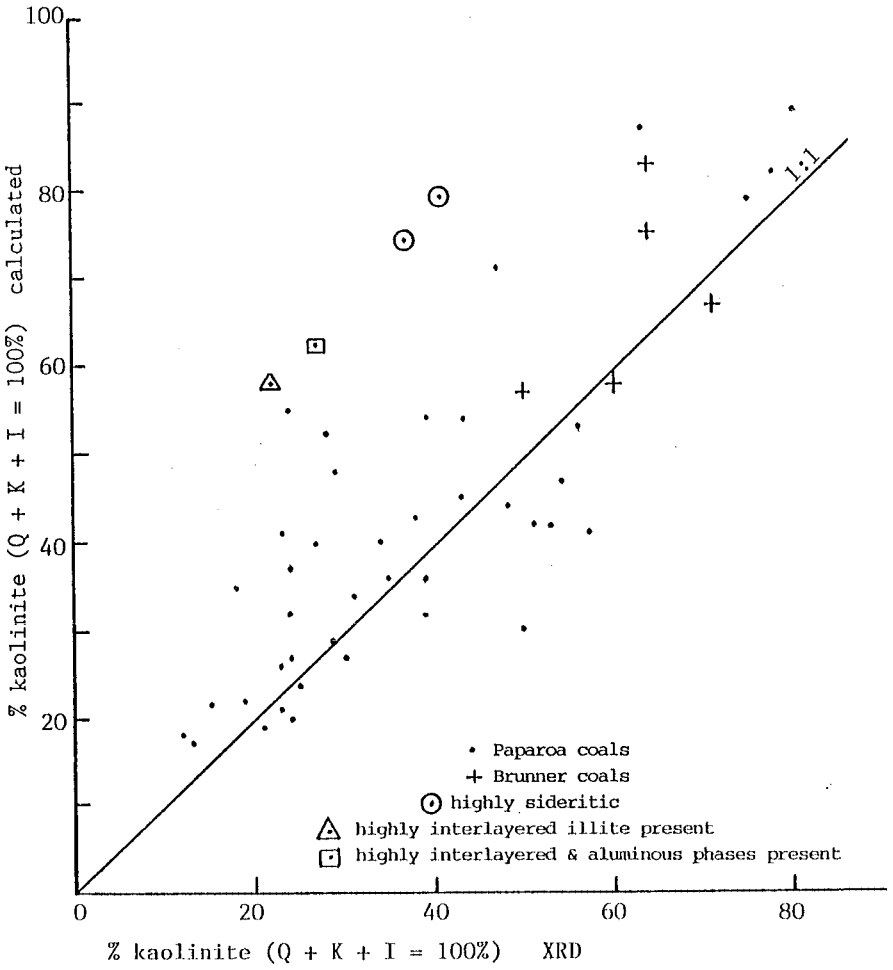


Figure 4.9 Comparison of kaolinite values expressed as Quartz + Kaolinite + Illite = 100%, determined by XRD and calculation from ash constituents analysis.

Table 4.2 Sample description and mineral data for Paparoa coals.

GREYMOUTH COALFIELD

Mineral Symbols: Q quartz Chl chlorite A aragonite K kaolinite C calcite Dw dawsonite I illite D dolomite R rutile Bm boehmite S siderite Cr crandallite

Sample Symbols: W whole seam channel or drillcore P ply CP composite of plies S spot R run-of-mine SG specific gravity fraction

	SAMPLE DESCRIPTION	SAMPLE TYPE	ASH% a.d.	MINERAL ASSEMBLAGE (XRD)	PRINCIPAL SILICATES, NORMALISED TO 100% (XRD) Quartz	Kaolinite	Illite	CALCULATED Quartz	Kaolinite	Illite
Morgan Member										
P1	Liverpool #3 Mine, Morgan Seam 0.8m from roof	S	4.4	K>>Q>I>Cr	19	67	14		n.d.	
P2	" " 1.0m from roof	S	1.4	K>S>>Q..I	18	64	18		n.d.	
P3	" " 1.2m from roof	S	2.9	K>Q>I	52	39	9	42	53	5
P4	" " 3.0m from roof	S	2.1	K>>Q>S>I	18	63	19	8	86	6
P5	" " 3.5m from roof	S	~2.0	K>Q>S>I	41	52	7		n.d.	
P6	" " mid seam	S	~6.5	K>Q>Cr	37	57	6		n.d.	
26/057	DH619 seaml, 1.0m upper ply	P	6.7	K..Q>P>I	48	49	3		n.d.	
26/058	" 1.8m middle ply	P	24.8	K..Q>I>D	40	40	20		n.d.	
26/059	" 1.5m lower ply	P	30.0	K>Q>>I	38	59	3		n.d.	
26/130	DH621 seam 2, upper coal ply	P	29.2	K>Q>I>P	34	53	13	35	42	23
26/132	" lower coal ply	P	30.1	Q>I>K>P	44	25	31	38	24	38
21/922	Liverpool Mine, run of mine 1979	R	7.7	n.d.		n.d.		27	37	36
27/156	" 1980	R	6.1	n.d.		n.d.		36	30	34
27/496	" 1981	R	5.9	n.d.		n.d.		27	32	41
30/337	" 1982	R	6.7	n.d.		n.d.		31	32	37
Rewanui Member										
P8	?Kimbell Seam, lower split; outcrop, Mt Davy	S	18.4	Q>K..I	47	24	28	43	27	30
P9	" " " "	S	11.4	Q>K>>I>R..Cr	58	34	8	51	39	10
P10	Kimbell Seam, Liverpool #3 Mine; seam roof	S	6.1	I>K>Q>S	8	18	74	15	28	57
P11	" " ~0.3m below roof	S	2.4	S>K>I>Q	22	41	37	6	77	17
P12	" " near floor	S	2.3	Q>K..S..I	44	27	29	39	38	23
P13	Unnamed seam, Mt Watson; blasted outcrop	W	3.8	K..Q>Cr>I..R	48	47	5	35	61	4
P14	?Kimbell Seam, ?Liverpool #1 workings, upper Seven Mile Creek	S	1.6	Q..I>K>S	40	22	38	21	58	21
P15	Unnamed seam, uppermost Seven Mile Creek; outcrop	W	~10	S>>Q>I>K	40	24	36	52	18	30
P16	Strongman Mine D Seam, 0.5m ply mid-seam	P	0.9	S>K>Q	~25	~75	<3	17	79	4
P17	Strongman Mine D Seam, 0.5m ply mid-seam	P	1.6	S>>Q>K	~65	~28	<5	44	52	4
P18	" ~0.5m below seam roof	S	2.0	K>S>Q>>I	~22	~78	<3	15	82	3
P19	" C Seam, silty roof coal	S	45.5	Q>I>S>>K	68	7	25	64	0	36
P20	" " near seam floor	S	6.4	Q>>K>I	87	12	3	79	18	3
P21	Unnamed seam, top of Rewanui Member, Seven Mile Ck; roof coal	S	13.5	I>K>>Q>Cr	<3	~43	~55	4	51	45
P22	As above, mid-seam	S	1.4	K>S>>I..Cr	<3	>95	<3		n.d.	
P23	As above, grab sample showing nodular siderite	S	11.3	S>>K>I>Q	15	56	29	22	53	25
21/913	Strongman Mine, run-of-mine 1979	R	5.1	n.d.		n.d.		39	25	36
27/487	" " 1980	R	3.6	n.d.		n.d.		33	24	43
30/329	" " 1982	R	5.9	n.d.		n.d.		33	25	42
37/016	" " 1985	R	2.9	S>Q>I>K>D>C	42	28	30	45	28	27
"	F1.3	R, SG	0.9					54	34	12

Table 4.2 continued.

GREYMOUTH COALFIELD

(Paparoa coals)

* NA Newman ash analysis ** Analysis applies to washed sample

SAMPLE DESCRIPTION	SAMPLE TYPE	ASH% a.d.	MINERAL ASSEMBLAGE (XRD)	PRINCIPAL SILICATES, NORMALISED TO 100%					
				Quartz (XRD)	Kaolinite (XRD)	Illite (XRD)	Quartz CALCULATED	Kaolinite CALCULATED	Illite CALCULATED
Rewanui Member, Rapahoe Sector Drillholes									
P24 DH624 seam 1, 1.0m ply mid-seam	P	~2.0	K>>Q>S	~20	~80	<3		n.d.	
P25 " " 1.0m ply near floor	P	~1.5	K>Q>I	30	51	19		n.d.	
P26 " seam 3, 0.5m ply near roof	P	~2.5	I..K>Q	18	39	43		n.d.	
P27 " " o.5m ply mid-seam	P	~4.1	K>>Q>I	17	73	10		n.d.	
26/060 DH619 seam 3 composite (1.4m)	W	4.5	Q..P>K>S>I	66	24	10	53	37	11
26/361 DH628 seaml ply 3 (1.0m)	P	2.1	S>Q>>K	~71	~29	<3	48	48	4
26/362 " ply 4 (0.1m)	P	22.4	Q>K>Cr..R>I	69	23	8	63	21	13
26/363 " ply 5 (1.1m)	P	1.5	S>Q>K..Cr	~63	~37	<3	21	74	5
26/374 " ply 16 (0.1m)	P	60.1	I>Q>K	34	21	45	36	19	45
26/376 " composite (10.65m)	W	3.2	Q>S>K>I	45	31	24	40	34	26
26/653 DH633 seam 1 ply 7 (1.55m)	P	1.9	K>Q>P>>I	41	54	5	44	47	9
26/654 " ply 8 (1.15m)	P	3.7	Q>K>P>I	61	39	<3	64	32	4
26/657 " ply 11 (0.25m)	P	4.4	Q>K>P>I	~62	~38	<3	55	43	2
26/662 " composite (10.3m)	W	5.8	Q>K>P>I	74	23	3	69	26	5
26/695 DH635 seam 5 composite (3.7m)	W	7.5	S>K>Q..P..I	31	51	18	27	42	29*
26/860 DH636 seam 3 composite (12.1m)	W	8.5	Q>I>K>D>S>>R	60	15	24		n.d.	**
29/026 DH646 seam 1 composite (14.3m)	W	1.7	Q>K>>I	57	39	~4	43	36	21
29/033 DH646 seam 2 composite (5.0m)	W	3.4	S>Q>K>I	74	23	~3	52	41	7
29/230 DH648 seam 1 composite (5.2m)	W	4.5	K..Q>I..S	47	50	~3	65	30	5
29/235 DH648 seam 2 composite (2.6m)	W	3.6	S>Q>K>>I	67	30	~3	48	27	25
29/019F DH633 seam 1 upper composite. Floats 1.35	SG	2.3	K>Q>>S>I	35	58	7		n.d.	
29/019F " " Floats 1.45-sinks 1.40	SG	12.3	Q>K>I..S>>R	43	33	24		n.d.	
29/019F " " Floats 1.55-sinks 1.50	SG	25.9	Q..I>K>S>>R	35	28	37		n.d.	
Dunollie Member									
P28 Exposed seam near old Point Elizabeth workings	S	~10	K>Q>I..R	~38	57	5	56	41	3
P29 " "	S	12.3	K>>I>R..Cr		n.d.			n.d.	
P30 Tiller Mine, Seven Mile Creek: main seam	W	3.6	P..S>K>>I..Q	~11	~80	~9	3	89	8
P31 " " 0.4m rider seam	W	5.8	K>Q>I	33	43	24	29	45	26
P32 " " uppermost Dunollie seam, silty	W	27.3	K>Q>P..I>C	33	48	19	36	44	20

Table 4.2 continued.

PIKE RIVER COALFIELD

(Paparoa coals)

SAMPLE	DESCRIPTION	SAMPLE TYPE	ASH% a.d.	MINERAL ASSEMBLAGE (XRD)	PRINCIPAL SILICATES, NORMALISED TO 100% (XRD) Quartz	Kaolinite	Illite	CALCULATED Quartz	Kaolinite	Illite
P33	Top of seam '7A', Member 4 (later included in 27/227)	S	1.7	K..Bm..I..Chl>S..Q>R		n.d.[1]		0	84	16[2]
P34	Thick Member 3 seam, later sampled as 27/679–27/681 — 3m mid-seam	P	19.2	Q>K>>Cr>R>I		n.d.[1]		7	67	26
P35	Thick Member 3 seam, later sampled as 27/679–27/681 — uppermost 2m	P	18.4	Q>K>I>Cr>>Bm	~82	~13	~5	77	17	6
P36	Thick Member 3 seam, later sampled as 27/679–27/681 — clarodurain horizon in P34	S	27.8	Q>K>Cr>I	~81	~15	<5	76	22	2
27/534	Uppermost Member 4 seam	W	10.5	I>Q>K>C>S	36	24	40	32	20	49
27/673	Upper Member 4 seam, lower split	W	2.2	Q>K..I>C>D>Cr	53	24	23	24	55	21
27/713	Member 3 seam, basal ply	P	5.6	Q>K>I>S>>Cr	53	35	12	46	36	18
30/172	Member 3; middle ply of thick seam	P	25.6	Q>K>I>D>R	50	37	13		n.d.	
27/282	Member 3 thick seam "3C" — top ply (1.4m)	P	6.1	Q>K..I	45	28	27		n.d.	
27/286	Member 3 thick seam "3C" — ply, mid-seam (1.7m)	P	19.1	K>Q>Cr>>I	~46	~54	<3		n.d.	
27/284	Member 3 thick seam "3C" — basal ply (1.4m)	P	7.7	Q>>I>>K	~76	<3	~24		n.d.	
27/531	Lower Member 4 seam	W	6.9	n.d.		n.d.		32	34	34
27/531S	" " Sinks 1.3	S.G.	34.9	I>Q>K>>D	23	19	58	39	22	39
27/531F	" " Floats 1.3	S.G.	3.0	n.d.		n.d.		18	56	26
27/531F	" " Floats 1.3–Sinks 1.26	S.G.	13.5	n.d.		n.d.		30	31	39[2]
27/531F	" " Floats 1.26–Sinks 1.24	S.G.	2.4	I>Q>K>D>Dw>Bm	19	27	54	16	62	22[2]
27/531F	" " Floats 1.24	S.G.	1.8	n.d.		n.d.		0	79	21[2]

Notes: 1. XRD sample not representative of bulk sample. 2. Calculated assemblage distorted by presence of highly interlayered illite and boehmite ± dawsonite.

Table 4.3 Sample description and mineral data for Brunner coals.

GREYMOUTH COALFIELD

SAMPLE DESCRIPTION	SAMPLE TYPE	ASH% a.d.	MINERAL ASSEMBLAGE (XRD)	MINERALS NORMALISED TO 100% (XRD) Quartz	Kaolinite	Illite	Boehmite	CALCULATED Quartz	Kaolinite	Illite	Boehmite
B1 Birchfield Opencast, grab sample from bins	S	6.7	K>P	-	>95	-	-	0	96	0	4
B2 " 0.2m rider seam	S	15.8	P>>K>Q>I					19	65	16	0
B3 " 0.05m below roof	S	2.0	P>K	-	>95	-	-	0	78	8	14
B4 " 0.1m below roof	S	2.6	n.d.					0	87	5	8
B5 " 0.5m below roof	S	1.7	n.d.					0	94	2	4
B6 " 2.0m below roof	S	2.0	P..K	-	>95	-	-	0	91	1	8
B7 " 3.0m below roof	S	2.1	P..K	-	>95	-	-	0	91	2	7
B8 " near floor	S	16.7						0	44	56	0
B9 1.5m seam near Spring Creek Bridge	W	7.8	K>P					1	96	3	0
B10 Coal Pit Heath Mine, unlocated specimen	S	2.3	Bm>Dw>>K	-	<5	-	>95	0	2	2	96*
B11 Brunner Mine portal, top half of seam	P	5.8	K>Bm>>Chl..Cr	-	64	-	36	0	83	2	15
B12 " " " lower half of seam	P	4.3	Bm..Dw..K	-	64	11	25	0	72	5	23*
B13 " " , block of stony coal, old bins	S	28.4	K>Bm..I>>Chl	-	50	16	34	0	57	30	13
B14 Tyneside Mine, near old portal; top half of seam	P	5.3	Bm..K>I..Dw					0	53	6	41*
B15 " " " " " lower half of seam	P	4.5	Bm>>K>Dw	-	<5	-	>95	0	2	5	93*
B16 Coolgardie Mine, unlocated specimens, low ash	S	9.4				n.d.		0	34	10	56
B17 " " " " high ash	S	54.5	K>I>Bm	-	71	17	12	0	67	21	12
B18 " " " " high ash	S	47.5	K>>I>Bm			n.d.		0	80	16	4
B19 Dobson Mine, unlocated specimens, low ash	S	3.3	D..Bm>K..Dw			n.d.		0	41	2	57*
B20 " " " " high ash	S	21.8	A>C>D>Bm	-	-	-	>95	0	37	3	60
B21 New Braehead Mine, top 0.5m	S	12.0	P>>K>Q	~40	~60	<5	-	30	58	12	0
B22 " " " bottom 0.5m	S	8.1	P>>K	-	>95	-	-	0	90	3	7
B23 " " " silty floor	S	56.6	K>I..Q					24	48	28	0
B14 F Tyneside Mine, as above Floats at 1.3	P,SG	3.7	Bm>D>K..Dw..C			n.d.		0	35	4	61*
29/017 S1.35-F1.4 DH644, Seam 2	W,SG	6.4	K>>Q..P..I			n.d.				n.d.	
" F1.3 "	W,SG	2.9	K>>P>I..Q			n.d.				n.d.	

*kaolinite-boehmite totals distorted by Dawsonite

Mineral Symbols

Q quartz Chl chlorite A aragonite K kaolinite C calcite Dw dawsonite I illite D dolomite
R rutile Bm boehmite S siderite Cr crandallite P pyrite

> more abundant than; >> much more abundant than; .. approximately equal to;

Sample Symbols

W whole seam channel or drillcore P ply CP composite of plies
S spot R run-of-mine SG specific gravity fraction

Table 4.3 continued. PIKE RIVER COALFIELD

(Brunner coals)

SAMPLE	DESCRIPTION		SAMPLE TYPE	ASH% a.d.	MINERAL ASSEMBLAGE (XRD)	MINERALS NORMALISED TO 100% CALCULATED Quartz	Kaolinite	Illite	Boehmite
27/287	top ply of 3	Outcrop	P		P>Q>K	n.d.			
27/288	middle ply of 3	"	P	3.0	Q>P>K..I	49	22	29	0
27/289	bottom ply of 3	"	P	8.6	Q>K	74	22	4	0
30/120	top 5.0m of 10.7m	"	P	4.6	P..Q>D>C..K	65	18	17	0
30/121	bottom 5.7m of 10.7m	"	P	3.6	D>P..C>>K>Q	34	49	17	0
30/971	Top ply Drillhole 6		D	7.0	P>C>D>Q	0	80	17	3
30/985	middle ply, Drillhole 6		D	3.1	D>P>Q>K	60	12	28	0
33/045	bottom ply Drillhole 6		D	5.1	Q>D>>K..I>C	83	8	9	0
33/006	Bottom composite, Drillhole 3		CD	2.7	D>>C>Q..P	0	53	16	31
30/121S	Sinks at 1.3		SG	23.3	D>>C>P..Q	53	19	28	0
30/121F	F1.3-S1.26		SG	0.4	D>>P..C..K	0	70	28	0
30/121F	F1.26-S1.24		SG	0.3	n.d.	0	68	23	9
31/121F	Floats at 1.24		SG	0.4	n.d.	0	53	21	26

Mineral Symbols

Q quartz Chl chlorite A aragonite K kaolinite C calcite Dw dawsonite I illite D dolomite
R rutile Bm boehmite S siderite Cr crandallite P pyrite

> more abundant than; >> much more abundant than; .. approximately equal to;

Sample Symbols

W whole seam channel or drillcore P ply CP composite of plies
S spot R run-of-mine SG specific gravity fraction

Table 4.3 continued.

BULLER COALFIELD

(Brunner coals)

SAMPLE	DESCRIPTION	SAMPLE TYPE	ASH% a.d.	MINERAL ASSEMBLAGE (XRD)	MINERALS NORMALISED TO 100% CALCULATED Quartz	Kaolinite	Illite	Boehmite
B24	Stockton Opencast, seam channel	W	0.3	Q>K>>I	62	26	12	0
B25	" " top 1m	P	0.5	Q>I>K>>Chl	65	16	19	0
B26	Webb Opencast, high ash band mid-seam	S	61.6	I>>K>>Q	<1	9	>90	0
B27S	Baynes Barren Belt, high ash coal; sinks 1.36	SG	45.2	K..I>Bm>>Chl>P	0	44	43	13
B27F	" " " " " " floats 1.36	SG	6.0	Bm>K>I>R	0	39	30	31
B28	Mt William Mine, mid-seam	S	0.2	K>Chl>I>R	39	44	17	0
27/510	Escarpment Mine, run-of-mine	R	1.8	K..P>Q>I	9	82	9	0
27/511	Sullivan Mine, run-of-mine	R	3.6	P>K>Q>I	32	54	14	0
37/040	" " " "	R	6.7	K>I..P>Bm>Chl		n.d.		
27/170	Webb Mine, run-of-mine	R	1.4	n.d.	0	60	35	5
30/349	" " " " "	R	1.7	n.d.	47	10	43	0
37/039	Charming Creek Mine, run-of-mine	R	2.4	K>I>Q..P..C			n.d.	
31/110	Webb/Baynes Block, DH 1241, top composite (2.3m)	CP	1.6	P>>I>Q>R+	0	34	49	17
31/111	" " " middle composite (5.0m)	CP	0.36	P>Q>I>K	32	19	49	0
31/112	" " " bottom composite (2.9m)	CP	2.8	P>K..I>Q	10	23	67	0
31/043	" " DH UG6 plies 3-8 (3.6m)	CP	1.5	K>P>Chl..Bm>I>R	0	93	4	3
31/044	" " DH 1215 top composite (2.4m)	CP	0.88	K..P>Chl..Bm>I>R	0	73	14	13
31/088	" " DH 1227 top composite (2.0 m)	CP	33.5	K>I..Chl			n.d.*	
29/936	" " DH UG4 Ply 6 (0.6m)	P	24.4	K>>I>>Chl	0	53	45	2
29/937	" " " " Ply 7 (0.6m)	P	2.6	K>>I..Bm	0	84	9	7
29/939	" " " " Ply 9 (0.6m)	P	0.7	n.d.	0	83	15	2
29/940	" " " " Ply 10 (0.6m)	P	0.3	n.d.	0	87	12	1

Mineral Symbols

+abundant iron oxide *major chlorite & expandable component

Q quartz Chl chlorite A aragonite K kaolinite C calcite Dw dawsonite I illite D dolomite
R rutile Bm boehmite S siderite Cr crandallite

> more abundant than; >> much more abundant than; .. approximately equal to;

Sample Symbols

W whole seam channel or drillcore P ply CP composite of plies
S spot R run-of-mine SG specific gravity fraction

Table 4.3 continued.

REEFTON GARVEY CREEK AREA, FLAT CREEK COALFIELD, INANGAHUA AREA

(Brunner coals)

SAMPLE DESCRIPTION		SAMPLE TYPE	ASH% a.d.	MINERAL ASSEMBLAGE (XRD)	MINERALS NORMALISED TO 100% Quartz	Kaolinite	Illite	Boehmite
					CALCULATED			
Reefton-Garvey Creek Area								
B35	Island Block, Drillhole 113 upper seam	S	7.8	K>Q..I>P>Cr	28	32	40	0
B36	" Drillhole 114 " "	S	5.5	K>Apatite>P..Cr..I>Q	32	35	33	0
B37	" Drillhole 113 basal seam	S	2.0	P>Q..I..K		n.d.		
21/930	Island Block Opencast	R	1.4	n.d.	10	74	16	0
27/503	" " "	R	2.4	n.d.	30	41	29	0
30/344	" " "	R	3.4	n.d.	24	44	32	0
B41	Burkes Creek Mine, #4 seam	R	2.1	Q>K>P>D>R	50	46	4	0
B42	Hyde & Party	R	9.1	Q>K>P>D	51	49	0	0
37/033	Waitahu Coal Pty (Dauntless Mine)	R	2.2	P>K>I>Q			n.d.	
Flat Creek Coalfield								
B45	Face sample, old opencast	W	1.6	P>K..I..Q*	25	43	32	0
Inangahua Area								
27/167	Heaphy Opencast Mine	R	3.6	n.d.	38	26	36	0
27/507	" " "	R	3.3	P>Q>C>K>I	37	46	17	0
30/349	" " "	R	4.0	n.d.	70	12	18	0
B48	Fletcher Creek Opencast	R	3.3	K>Q	0	57	12	31
37/035	Burley's Opencast	R	5.4	Q>K			n.d.	

Mineral Symbols

* ankerite is known to occur in other samples

Q quartz Chl chlorite A aragonite K kaolinite C calcite Dw dawsonite I illite
D dolomite R rutile Bm boehmite S siderite Cr crandallite P pyrite

>more abundant than; >> much more abundant than; .. approximately equal to;

Sample Symbols

W whole seam channel or drillcore P ply CP composite of plies
S spot R run-of-mine SG specific gravity fraction

Table 4.4 Calculated mineral assemblages for Paparoa coals, normalised to 100%. Refer to Table 4.2 for sample locations.

GREYMOUTH COALFIELD

Sample	A%	Qtz	Kaolin.	Illite	Rutile	Sid.	Cal.	Crand.
P3	2.9	38.3	48.6	4.9	3.0	3.1	0.2	1.8
P4	2.1	6.5	71.4	5.3	6.2	7.5	0.1	3.0
P8	18.4	39.8	25.0	28.1	2.9	3.2	0.0	1.0
P9	11.4	46.5	35.8	9.6	3.3	2.5	0.0	2.4
P10	6.1	11.8	22.6	45.4	1.0	6.2	0.6	12.3
P11	2.4	2.6	34.9	7.8	2.3	51.3	0.0	1.1
P12	2.3	29.4	29.1	17.4	1.2	17.9	2.5	2.5
P13	3.8	24.7	43.8	2.9	8.3	2.2	0.0	18.0
P14	1.6	17.3	46.3	16.5	1.3	17.2	1.1	0.4
P15	12.4	2.9	1.0	1.7	0.1	92.6	0.0	1.7
P16	0.9	7.8	36.4	1.8	0.5	53.3	0.0	0.3
P17	1.6	16.6	19.7	1.4	0.4	61.6	0.0	0.3
P18	2.0	10.8	58.0	1.9	0.6	28.5	0.0	0.2
P19	45.5	53.9	0.0	29.8	0.8	12.0	0.0	3.5
P20	6.4	76.5	17.4	3.4	1.3	0.9	0.0	0.5
P21	13.5	3.9	43.3	38.3	1.3	5.1	0.0	8.1
P23	11.3	2.4	5.6	2.7	0.2	88.7	0.0	0.3
P28	13.0	48.2	35.6	2.9	5.5	2.0	0.2	5.6
P30	3.6	1.2	34.2	2.9	0.5	60.9	0.0	0.3
" S1.5	51.2	2.0	21.5	3.1	0.1	73.1	0.0	0.2
" F1.5-S1.3	1.5	0.0	60.5	3.7	1.0	32.2	0.0	0.8
" F1.3	0.8	0.0	59.6	3.3	2.8	29.4	1.8	0.7
P31	5.8	23.0	35.9	21.2	1.6	15.6	0.9	1.8
P32	27.3	29.4	35.1	16.4	1.4	17.5	0.0	0.2
26/130	29.2	31.6	38.4	20.9	2.0	6.9	0.0	0.3
26/132	30.1	34.2	22.1	34.9	1.1	7.5	0.0	0.1
21/922	7.7	22.0	29.3	29.2	2.3	14.7	1.2	1.3
27/156	6.1	25.2	21.6	24.1	2.8	8.8	5.1	12.3
27/496	5.9	19.7	24.0	30.8	2.3	17.0	1.0	5.3
30/337	6.7	24.6	25.4	29.7	2.5	7.0	0.8	10.0
21/913	5.1	28.3	17.8	25.9	0.9	23.8	2.1	1.2
27/487	3.6	22.3	16.8	29.2	0.8	22.1	5.2	3.6
30/329	5.9	25.6	19.3	32.2	0.9	18.5	0.6	3.0
37/016	2.9	29.0	18.1	17.4	0.9	33.4	0.0	1.2
" S1.5	53.2	20.7	9.6	19.5	0.4	48.7	0.0	1.1
" F1.5-S1.3	7.4	36.4	25.4	17.5	0.9	16.3	1.8	1.8
" F1.3	0.9	46.5	29.6	10.5	1.8	9.4	0.9	1.4

PIKE RIVER COALFIELD

	Sample	A%	Qtz	Kaolin.	Illite	Rutile	Sid.	Cal.	Crand.	Pyrite
	P33	1.7	0.0	44.8	8.6	1.3	41.3	3.2	0.3	
	P34	19.2	7.2	63.1	24.1	1.4	2.5	0.3	1.4	
	P35	18.4	72.3	16.4	5.6	1.0	2.0	0.3	2.3	
	P36	27.8	69.6	19.9	2.2	1.2	1.3	0.0	5.7	
	27/534	10.1	28.5	17.8	43.7	1.3	0.0	3.5	1.3	3.8
	27/535	4.2	25.9	32.5	13.0	1.2	0.0	5.8	2.5	19.0
	27/537	7.6	29.8	21.8	14.4	1.0	32.8	0.0	0.2	0.0
	27/541	6.7	29.2	46.9	8.7	4.1	0.0	5.5	1.2	4.4
	27/543	15.1	50.8	29.0	9.1	5.8	3.6	0.4	1.2	0.0
	27/544	6.9	27.1	41.0	15.3	3.4	10.0	0.8	2.3	0.0
	27/673	2.5	18.0	41.6	16.2	1.2	18.9	3.9	0.3	0.0
	27/707	7.3	23.2	51.0	6.2	5.9	6.9	1.5	5.4	0.0
	27/708	3.7	23.7	43.9	10.0	2.1	0.0	9.8	0.9	9.6
	27/713	5.2	42.1	33.3	16.5	2.9	0.0	1.6	1.9	1.7
	30/119	8.9	52.2	27.3	9.2	2.4	0.0	3.0	1.0	5.0
	30/122	5.7	3.7	72.1	6.4	2.4	0.0	1.3	7.0	7.2
	30/123	9.5	29.0	52.9	8.8	4.3	0.0	1.2	0.5	3.4
	30/124	3.3	22.1	33.6	19.3	1.1	23.6	0.0	0.2	0.0
	30/156	6.9	38.0	36.1	17.6	1.4	6.6	0.0	0.2	0.0
	30/179	6.8	29.3	41.5	24.2	1.0	3.7	0.0	0.3	0.0
	30/182	8.6	60.3	23.4	8.2	1.7	0.0	1.2	3.1	2.1
	27/531	6.9	26.6	28.0	28.4	1.8	11.5	2.3	1.5	0.0
27/531	S 1.3	34.9	34.8	19.3	35.0	1.2	8.0	1.2	0.5	0.0
"	F 1.3	3.0	13.4	41.5	19.1	2.7	16.3	3.7	3.3	
"	F1.3-S1.26	13.5	24.6	25.2	32.4	1.7	12.2	2.3	1.6	
"	F1.26-S1.24	2.4	12.3	46.8	16.9	3.6	9.9	5.3	5.2	
"	F 1.24	1.8	0.0	40.4	10.9	2.4	33.0	5.1	1.6	

A = ash% air dried basis Qtz = quartz Kaolin = kaolinite Sid = siderite
Cal = calcite Crand = crandallite

GREYMOUTH COALFIELD

Sample	A%	Qtz	Kaolin.	Illite	Boehm.	Rutile	Dol.	Cal.	Crand.	Pyrite
B1	6.7	0.0	54.6	0.1	2.3	0.2	1.5	1.4	0.1	39.9
B2	15.8	2.9	10.3	2.6	0.0	0.5	0.6	0.7	0.1	82.2
B3	2.0	0.0	19.0	1.9	3.3	0.3	4.1	7.7	0.1	63.6
B4	2.6	0.0	15.2	0.9	1.4	0.1	2.3	4.6	0.0	75.5
B5	1.7	0.0	70.5	1.6	3.0	0.6	3.9	6.4	0.1	14.0
B6	2.0	0.0	42.0	0.6	3.7	0.2	3.7	3.1	0.0	46.7
B7	2.1	0.0	45.3	0.8	3.7	0.6	2.8	3.3	0.5	43.0
B8	16.7	0.2	38.0	49.1	0.0	7.3	2.5	0.0	0.6	2.2
B9	7.8	1.0	69.5	2.5	0.0	0.2	2.1	0.8	0.2	23.9
B10	2.3	0.0	1.6	1.5	77.3	0.2	9.4	9.2	0.2	0.6
B11	5.8	0.0	73.0	1.8	12.7	0.2	5.5	1.1	4.0	1.6
B12	4.3	0.0	53.9	3.4	17.2	0.3	18.7	0.0	0.4	6.1
B13	28.4	0.0	51.6	27.8	11.7	2.9	4.4	0.0	0.5	1.1
B14	5.3	0.0	34.5	3.7	26.8	0.2	18.8	0.0	2.3	13.7
" Fl.4 Sl.3	6.3	0.0	42.9	3.2	23.8	0.1	14.5	0.0	2.7	12.7
" Fl.3	3.7	0.0	21.6	2.5	37.4	0.1	24.1	0.0	1.9	12.4
B15	4.5	0.0	1.7	4.2	73.8	0.1	15.8	0.0	1.6	2.9
B16	9.4	0.0	28.0	8.7	46.8	5.0	5.6	0.0	5.0	0.9
B17	54.5	0.0	63.7	20.3	11.3	1.6	1.7	0.0	0.4	1.1
B18	47.5	0.0	76.1	15.7	3.6	1.3	1.8	0.0	0.3	1.1
B19	3.3	0.0	24.2	1.5	33.7	0.3	31.3	1.9	0.4	6.7
B20	21.8	0.0	2.5	0.2	4.1	0.0	19.1	73.9	0.0	0.2
B21	12.0	6.3	12.5	2.6	0.0	0.4	1.5	2.6	0.0	74.0
B22	8.1	0.0	10.4	0.3	0.8	0.1	2.2	4.6	0.0	81.6
B23	56.6	18.4	37.2	21.6	0.0	3.0	1.4	0.0	0.0	18.4

PIKE RIVER COALFIELD

Sample	A%	Qtz	Kaolin.	Illite	Boehm.	Rutile	Dol.	Cal.	Crand.	Pyrite
30/792	5.3	2.6	3.3	3.0	0.0	0.2	47.1	8.5	0.0	35.3
30/793	2.4	0.8	5.4	1.5	0.0	0.1	68.8	11.7	0.1	11.6
30/927	4.2	11.8	2.3	3.6	0.0	0.1	47.3	0.1	0.1	34.8
30/928	3.1	2.5	0.8	1.7	0.0	0.1	78.1	4.9	0.0	11.9
33/003	4.8	11.3	6.8	6.8	0.0	0.3	32.7	5.7	0.1	36.3
33/004	3.5	4.8	2.5	0.9	0.0	0.1	71.8	14.8	0.0	5.1
33/005	3.0	3.4	1.1	1.3	0.0	0.1	77.6	3.5	0.1	12.9
33/006	2.7	0.0	3.1	0.9	1.8	0.1	83.0	6.6	0.0	4.6
30/948	3.9	14.8	4.5	2.6	0.0	0.3	48.6	9.9	0.1	19.2
30/966	5.5	4.6	2.0	3.5	0.0	0.1	74.0	4.3	0.0	11.6
33/044	7.2	17.5	3.5	6.6	0.0	0.1	38.2	5.8	0.1	28.2
30/971	7.0	0.0	8.8	1.9	0.3	0.2	14.7	18.1	0.1	55.8
30/985	3.1	10.4	2.1	4.9	0.0	0.2	58.4	0.9	0.1	23.1
33/045	5.1	50.8	4.6	5.8	0.0	0.2	31.3	2.2	0.1	5.1
27/545	12.6	55.2	0.0	25.7	0.0	0.4	2.9	0.1	0.1	15.7
27/546	11.5	57.5	4.0	21.2	0.0	0.7	3.0	0.4	0.1	13.1
27/678	2.0	19.8	17.4	15.3	0.0	0.6	9.5	0.0	0.3	37.2
27/686	6.7	24.7	25.4	20.6	0.0	1.1	2.8	0.0	0.1	25.4
27/700	1.2	1.3	26.1	7.4	0.0	0.4	3.6	3.2	0.3	57.6
27/705	19.7	74.1	5.6	7.8	0.0	0.5	2.1	0.2	0.1	9.6
27/709	3.1	37.7	19.2	18.9	0.0	0.6	7.4	1.9	0.3	14.1
30/120	4.6	22.6	6.3	5.8	0.0	0.5	14.7	5.7	0.0	44.3
30/121	3.6	1.4	2.0	0.7	0.0	0.1	68.5	13.6	0.1	13.8
" Sl.3	23.3	1.4	0.5	0.7	0.0	0.0	72.9	13.3	0.1	11.1
" Fl.3 Sl.26	0.4	0.3	10.2	4.0	0.0	0.5	36.1	16.1	0.7	32.2
" Fl.26 Sl.24	0.3	0.0	11.0	3.7	1.4	0.6	28.9	21.8	0.5	32.0
" Fl.24	0.4	0.0	9.2	3.7	4.5	0.6	27.3	22.2	0.3	32.2
30/127	4.1	33.9	12.5	22.2	0.0	0.7	2.6	0.4	0.1	27.5
30/128	3.3	61.7	17.0	3.9	0.0	0.5	3.5	1.9	0.1	11.4
27/288	3.0	18.8	8.6	11.1	0.0	0.3	11.3	5.2	0.2	44.4
27/289	8.6	64.0	18.6	3.2	0.0	2.3	3.1	2.0	0.1	6.6
27/217	5.0	26.7	9.6	5.7	0.0	0.8	5.1	2.9	0.1	49.0
27/224	2.3	22.4	16.3	14.5	0.0	0.8	11.4	3.6	0.4	30.6

Table 4.5 Calculated mineral assemblages for Brunner coals.

Table 4.5 continued

Sample	A%	Qtz	Kaolin.	Illite	Boehm.	Rutile	Dol.	Cal.	Crand.	Pyrite
Buller										
B24	0.3	54.3	22.7	10.5	0.0	1.1	0.5	3.8	0.1	7.1
B25	0.5	51.4	13.0	14.8	0.0	0.4	5.6	1.0	0.1	13.8
B26	61.6	0.4	8.6	85.7	0.0	1.3	1.7	0.0	0.4	1.9
B27S	45.2	0.0	40.9	40.0	12.2	1.5	1.5	0.0	0.6	3.3
B27F	6.0	0.0	34.7	27.4	28.2	3.5	1.9	1.5	1.0	1.7
B28	0.2	31.5	35.1	13.5	0.0	3.4	4.7	7.1	0.2	4.6
27/510	1.8	5.3	46.2	5.1	0.0	1.9	0.6	1.9	0.4	38.6
27/511	3.6	19.0	31.5	7.9	0.0	0.7	0.8	1.5	0.7	37.8
27/170	1.4	0.0	51.8	30.8	4.3	1.9	2.3	1.0	1.7	6.3
30/349	1.7	32.3	7.1	30.2	0.0	0.6	1.4	1.9	0.4	26.1
29/936	24.4	0.0	50.1	42.6	2.0	1.8	1.3	0.0	0.6	1.8
29/937	2.6	0.0	74.4	7.9	6.1	3.6	0.0	4.6	0.7	2.7
29/939	0.7	0.0	71.0	12.9	2.1	0.3	0.0	1.9	0.2	11.5
29/940	0.3	0.0	71.7	9.5	1.0	1.0	0.5	3.8	0.2	12.3
Reefton-Garvey Creek										
B35	7.8	18.2	21.0	26.1	0.0	1.2	2.7	0.4	10.6	19.8
B36	5.5	13.1	14.3	13.5	0.0	0.8	1.3	18.2	30.6	8.1
B41	2.1	26.9	24.3	2.1	0.0	3.0	24.6	0.3	0.4	18.4
21/930	1.4	7.0	52.1	11.4	0.0	0.6	3.5	0.3	1.1	24.0
27/503	2.4	17.5	23.8	16.5	0.0	0.7	5.4	0.6	1.5	34.0
30/344	3.4	14.5	26.1	19.1	0.0	2.1	15.4	2.4	6.0	14.4
B42	3.3	27.1	25.9	0.2	0.0	3.0	24.6	0.3	0.4	18.4
Flat Creek										
B45	1.6	11.1	18.9	13.8	0.0	0.5	6.7	0.0	2.0	46.9
Inangahua area *										
27/167	3.6	3.9	2.6	3.6	0.0	0.2	40.4	36.3	0.3	12.8
27/507	3.3	7.8	9.6	3.6	0.0	0.4	35.7	27.3	1.0	14.6
30/347	4.0	17.2	3.0	4.3	0.0	0.2	25.1	24.3	0.3	25.6
B48	3.3	0.0	10.9	2.2	6.0	0.5	23.1	53.7	0.7	3.0

* assemblages for Inangahua coals are largely hypothetical. A large proportion of the mineral matter is organically bound.

CHAPTER 5

MODES OF OCCURRENCE OF INORGANIC CONSTITUENTS

5.1 INTRODUCTION

An important function of coal geochemistry is to determine the modes (mineral form or chemical environment, e.g., Finkelman, 1980) in which the inorganic components occur within the raw coal. To achieve this aim, the prime source of information is direct mineralogical analysis, but additional information is required to determine compositional trends which are not adequately revealed by the LTA-XRD procedure. Useful input is provided by graphs which reveal correlation between ash constituents, and by the mineralogy and composition of float-sink fractions.

The discussion in this chapter is based on the following evidence:

(i) General information from XRD and petrography.
(ii) Ash constituent interrelationships.
(iii) Graphical treatment of sink-float data (see 5.2).
(iv) Evidence from serial plies. Full seam intersections from Rapahoe Sector Drillholes 628 and 633 were analysed as serial plies. These analyses are discussed in detail in Chapter 6, but many of the graphs appearing in the present chapter have one or both of the drillhole ply sets identified by special symbols. Because of their narrow sample interval, the ply data frequently plot as extreme values.

5.2 SINK-FLOAT ANALYSES

A set of 5 coals were analysed in separate density fractions, prepared by sink-float separation of -1mm sample material in perchloroethylene/petroleum spirit mixtures. Various separation densities were chosen in an attempt to obtain a range of fractions suitable for ash constitu-

ents analysis. The samples, which were chosen to provide a range in coal character, displayed a wide variation in separation behaviour (Table 5.1).

Results of the chemical analyses are shown in Figures 5.1–5.4 and Table 5.2. Where possible, individual ash constituents have been plotted against reciprocal of ash %. Graphs of this type are useful for distinguishing between simple mixtures of mineral grains in coal, and inorganic material bound to or intimately combined with the organic coal substance. If the graph origin is zero for both axes, elements occurring within discrete mineral particles are increasingly concentrated in the sink fractions, and will show a decline relative to other elements as the value of 1/A% increases. Where linear trends can be recognised, extrapolation of such a plot to 100% ash (1/A – 0.01) yields the theoretical composition of 'pure minerals' associated with the coal.

5.2.1 Paparoa coal samples

Three contrasting Paparoa coal samples are represented. The Pike River sample (27/531, Figure 5.1) was separated into 4 density fractions, which were supplemented by cumulative floats at SG 1.3 , and by the raw sample, thereby providing a total of 6 fractions. The seam from which this sample was taken has mineralogical and petrographic characteristics which are atypical of Paparoa coals.

With the possible exception of the lightest fraction (F 1.24), the trends shown by analyses for 27/531 are well defined. Silica and K_2O progressively decline with ash, whereas all other components increase over this range. An increasingly aluminous and sodic composition for ash in the light fractions is reflected by the identification of boehmite and dawsonite (Table 4.2).

These trends contrast strongly with those observed for the Strongman Mine coal (37/016, Figure 5.2). Compositional trends for this sample exhibit deviations, or inflections, in the medium–high ash region of the

Table 5.1 Ash and recovery data for sink-float fractions.

SAMPLE	S.G. fraction	% in fraction	%Ash (air dried)
Paparoa coals			
27/531 (Pike River Coalfield)	whole	100	6.9
"	F1.3	88.3	3.0
"	S1.3	11.7	34.9
"	F1.3-S1.26	3.3	13.4
"	F1.26-S1.24	59.8	2.4
"	F1.24	25.2	1.8
37/016 (Strongman Mine, Greymouth)	whole	100	2.9
"	S1.5	3.2	53.2
"	F1.5-S1.3	5.5	7.4
"	F1.3	91.2	0.9
P30, (Tiller Mine, Greymouth)	whole	100	3.6
"	S1.5	5.0	51.2
"	F1.5-S1.3	34.4	1.5
"	F1.3	60.6	0.8
Brunner coals			
30/121 (Pike River Coalfield)	whole	100	3.6
"	S1.3	10.0	23.3
"	F1.3-S1.26	32.5	0.4
"	F1.26-S1.24	23.0	0.3
"	F1.24	34.5	0.4
B14 (Greymouth Coalfield)	whole	100	5.3
"	S1.4	0.9	>50*
"	F1.4-S1.3	56.4	6.3
"	F1.3	42.7	3.7

* contaminated, not analysed

Table 5.2 Ash constituent analyses for sink-float fractions from sample 30/121 (Brunner seam, Pike River Coalfield).

Sample	A	MgO	Na_2O	SiO_2	Al_2O_3	SO_3	P_2O_5	Fe_2O_3	MnO	TiO_2	CaO	K_2O	Sr(ppm)	Ni(ppm)
30/121 (whole)	3.6	17.20	0.21	3.18	1.34	26.67	0.02	10.53	0.14	0.09	32.70	0.07	1941	172
30/121 S1.3	23.3	26.16	0.00	3.34	0.85	8.14	0.03	12.14	0.20	0.00	48.62	0.11	1392	19
" F1.3-1.24	0.4	8.13	1.82	8.00	6.56	29.90	0.24	22.15	0.17	0.48	20.69	0.37	3802	433
" F1.26-S1.24	0.3	6.09	2.45	7.49	7.52	29.56	0.18	20.60	0.09	0.58	20.37	0.32	5877	700
" F1.24	0.4	5.81	2.40	6.62	9.21	30.16	0.10	20.88	0.06	0.57	20.25	0.32	4952	963

Figure 5.1

Ash composition vs 1/Ash (dry basis) for sink-float fractions of sample 27/531 (Paparoa Coal Measures, Pike River Coalfield).

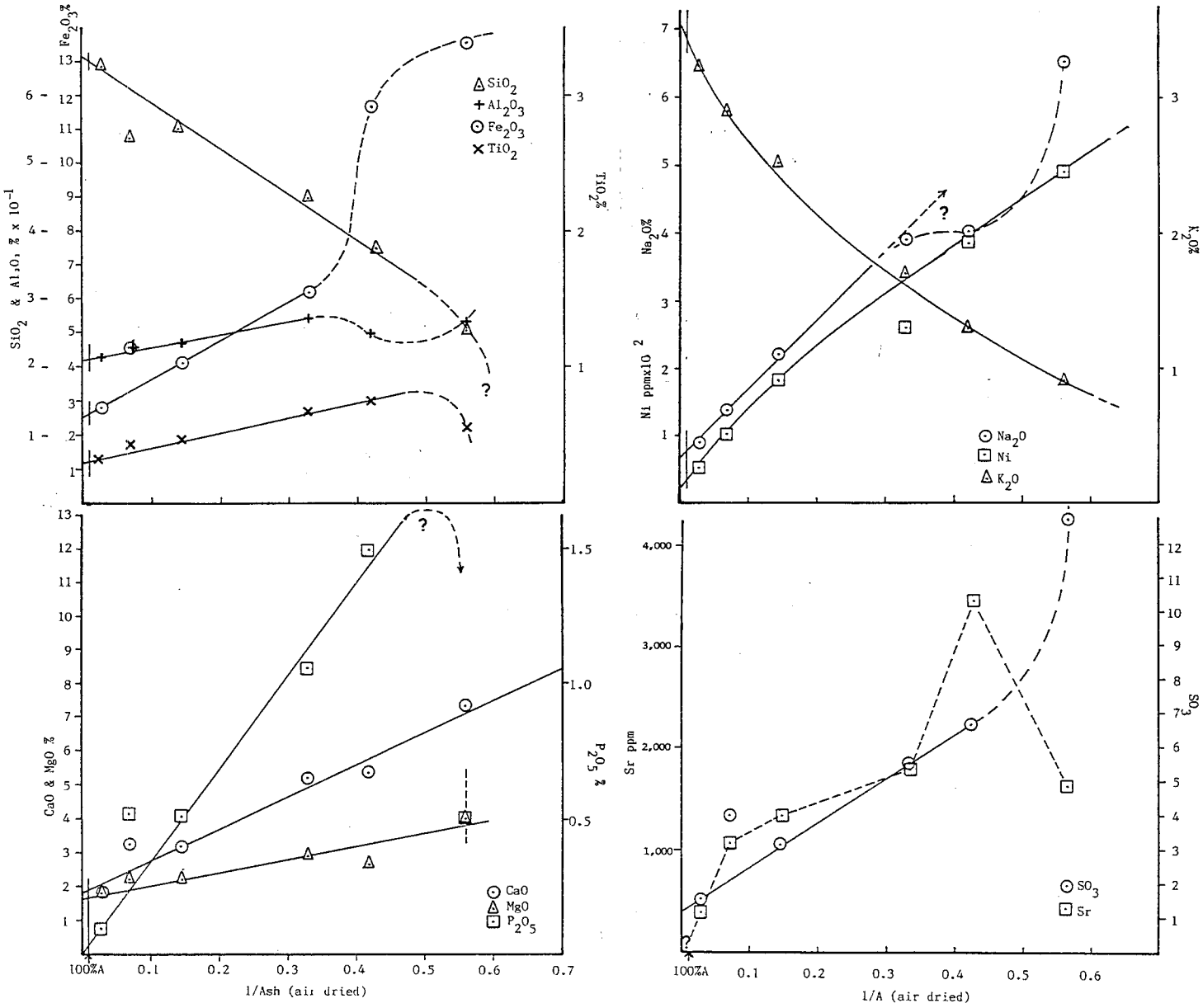


Figure 5.2

Ash composition vs 1/Ash (dry basis) for sink-float fractions of sample 37/016, Strongman Mine (Rewanui Member, Paparoa Coal Measures, Greymouth Coalfield).

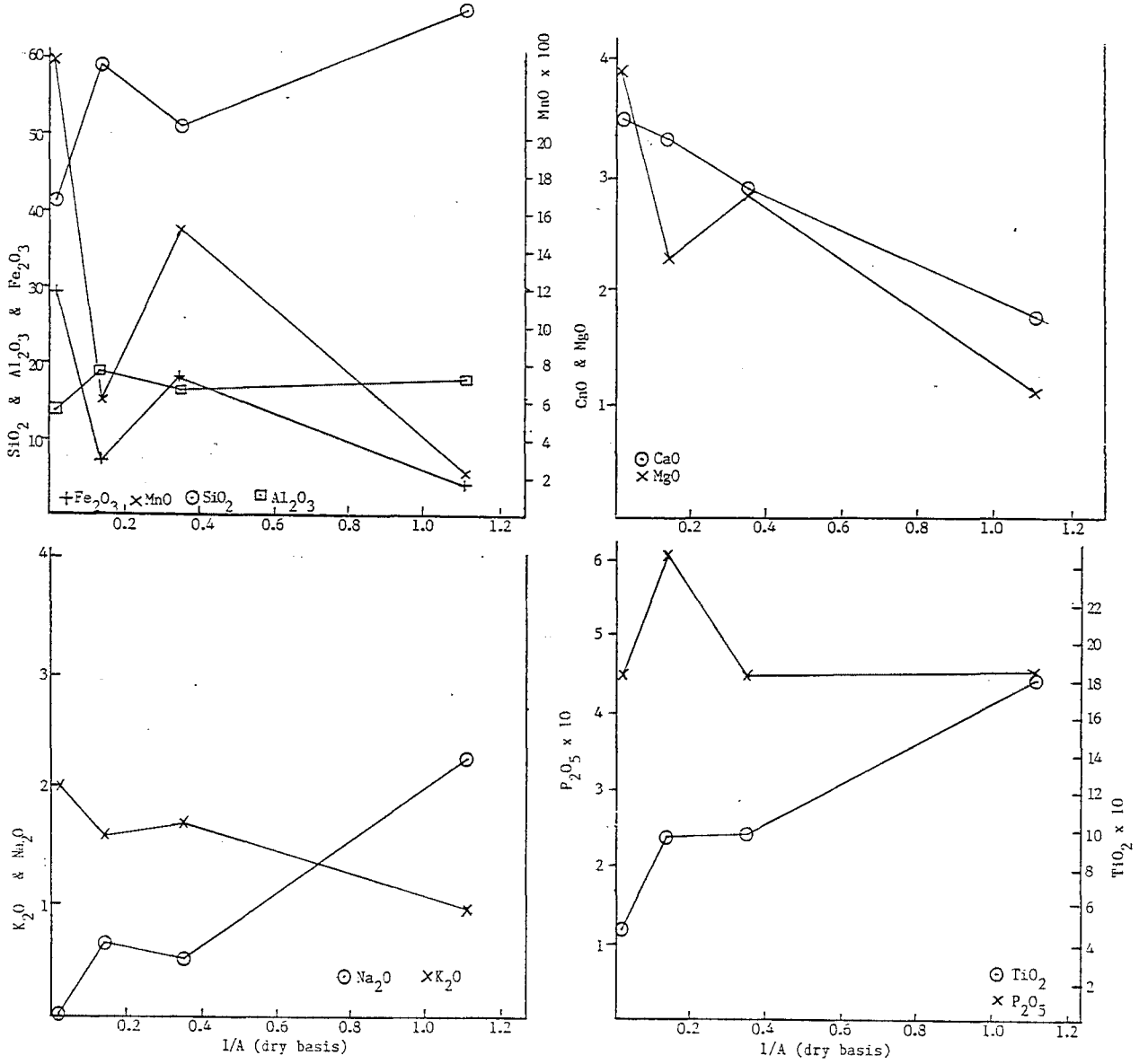
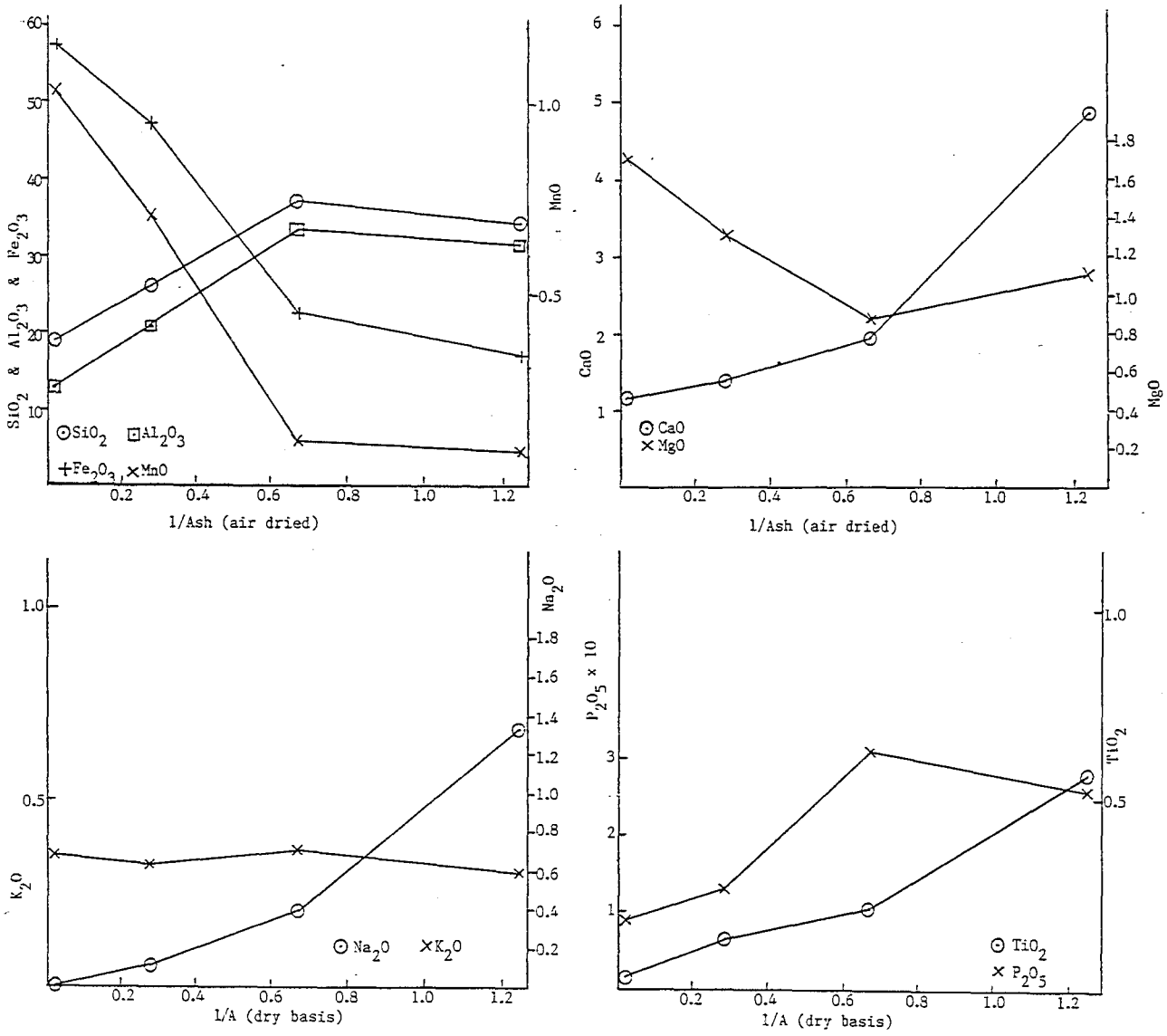


Figure 5.3

Ash composition vs 1/Ash (dry basis) for sink-float fractions of sample P30, Tiller Mine (Dunollie Member, Paparoa Coal Measures, Greymouth Coalfield).



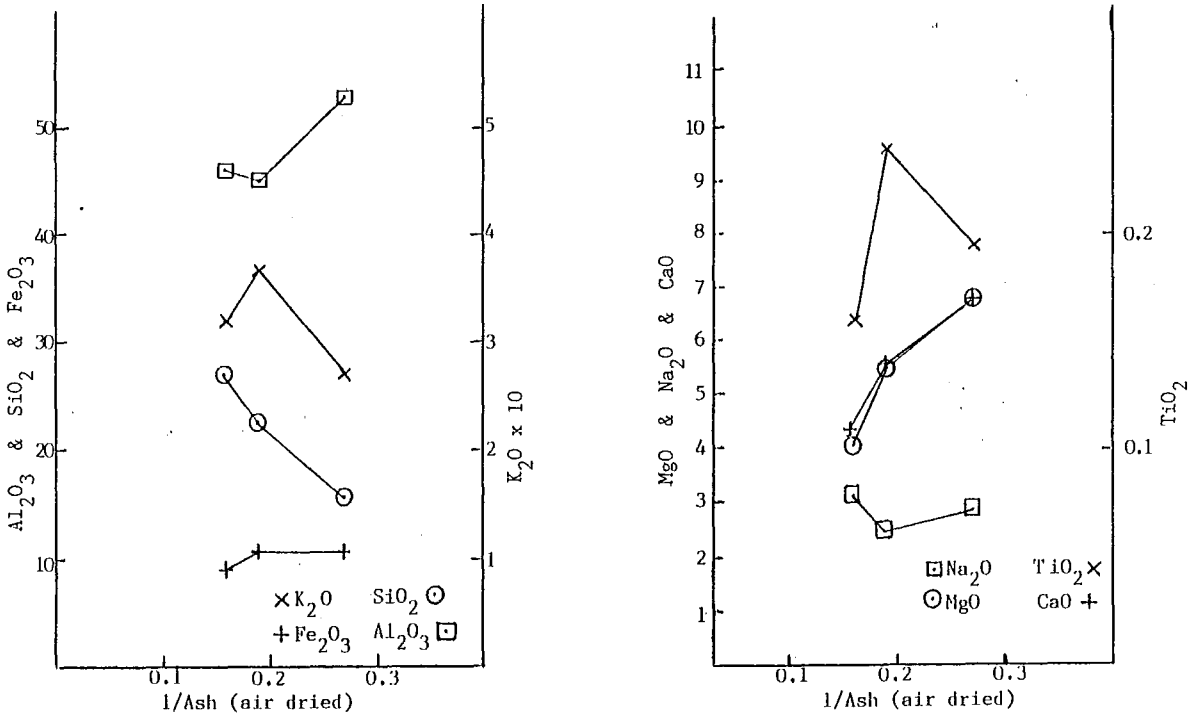


Figure 5.4 Ash composition vs 1/Ash (dry basis) for sink-float fractions of sample B14, Tyneside Mine (Brunner Coal Measures, Greymouth Coalfield).

plots. These inflections are considered to be a result of irregular separation behaviour arising from preferential removal of one mineral at a particular density. Despite this characteristic, the overall trends show that Fe_2O_3, MnO, MgO, CaO, and K_2O decline with ash, corresponding to the expected "washing out" of carbonate minerals and muddy sediment. However, the corresponding rise in SiO_2 as ash declines is not matched by a rise in Al_2O_3, suggesting that fine grained silica occurs in the low ash coal. This is confirmed by XRD of mineral matter from the F 1.3 fraction (Table 4.2), which shows abundant quartz. Some of this quartz is sufficiently fine grained to appear on the diffractogram of the -2µm LTA fraction (Figure 3.5). High silica in ash for float samples of Strongman coal has previously been recorded by Hughson (1939), during a brief investigation of ash fusion temperatures.

The third Paparoa sample (P30, Figure 5.3) was taken from the Tiller Mine, Greymouth, and represents coal from the Dunollie Coal Measures Member. Washed fractions for this coal show an extremely kaolinite-rich, quartz-poor characteristic, demonstrated by the parallel trends of SiO_2 and Al_2O_3, which both increase in response to the strong "washing out" of pyrite and siderite in the lighter fractions.

5.2.2 Brunner samples

Sample 30/121 (Brunner Seam, Pike River Coalfield) exhibited such a sharp separation of mineral matter from coal at SG 1.3 that there was little scope for further separation of the floats. The lightest fraction (F 1.24) produced an ash value similar to that of an intermediate fraction (F 1.3 - S 1.26), possibly as a result of large fluctuations in mineral matter/ash ratios. Because of these problems, the results for this sample are not graphed, but are presented in Table 5.2. If the fluctuation in ash is ignored, some systematic variation in ash composition can be recognised. As ash declines, the Al_2O_3/SiO_2 ratio increases and becomes hyperaluminous, whereas Fe_2O_3, CaO, and MgO all remain high and relatively constant in the low ash float fractions. Although the hyperaluminous fractions have not been analysed mineralogically, XRD results for LTA from the fraction F 1.3 - S 1.26 confirm the presence of pyrite, dolomite, and calcite as major mineral components.

The other Brunner sample (B14, Table 5.4) is taken from an area of strongly hyperaluminous coal in the Greymouth Coalfield. The S 1.4 fraction, which represented less than 1% of the raw sample, was found to include contamination from rocks and gravels overlying the seam at the sample site, and was not analysed. The other sink-float fractions for this sample reveal an extreme, intimate dispersion of mineral matter in the coal; there is little change in ash values between the raw sample and the two density fractions analysed. Geochemical trends for this sample are not well marked, except for SiO_2 and Al_2O_3, which diverge to produce an increasingly peraluminous composition as ash declines, and CaO and MgO, which both increase as ash declines. XRD results for the F 1.3 fraction (Table 4.3) show the presence of abundant boehmite, dawsonite, dolomite, and calcite.

5.3 SiO_2 and Al_2O_3

It is obvious that quartz, kaolinite and illite are the principal minerals contributing SiO_2, and that kaolinite and illite are the main

sources of Al_2O_3 in ash. Other silicate minerals, with the exception of minor chlorite, are unknown in the coals. However, crandallite is a significant source of Al_2O_3 throughout both Paparoa and Brunner coals, and both boehmite and dawsonite are common in some Brunner seams.

A general plot of Al_2O_3 against SiO_2 for Rapahoe Sector Paparoa samples (Figure 5.5) shows a very large variation in the ratio of these two components. None of the plotted points is more aluminous than illite (n = 1.5), despite a substantial kaolinite content for many samples, indicating a very strong quartz component in many of these coals.

A similar variation exists for Brunner coals, except that individual coalfields plot in more restricted fields, which may extend above the kaolinite line due to the presence of boehmite and dawsonite (Chapter 7).

5.4 Fe_2O_3 and MnO

5.4.1 Paparoa coals

If the potential occurrence of iron in illite is ignored, then only 4 iron-bearing minerals can be recognised in Paparoa coal, i.e. siderite, pyrite, marcasite, and chlorite.

Iron Sulphides. The quantity of iron sulphide present in a coal is conveniently measured by forms of sulphur measurement. There is no reason to believe that sulphate in Paparoa coals represents anything other than oxidised sulphide, except in special circumstances where accumulation of transported sulphate might occur. Total sulphide in the unoxidised sample is, therefore, indicated by combined sulphate plus pyritic sulphur, or total inorganic sulphur.

Available evidence suggests that the "primary" or vegetation-derived sulphur content of Paparoa coal is approximately 0.35%, as argued by Wellman (1952). This "primary" sulphur appears to be almost entirely organic. Forms of sulphur analysed in 12 run-of-mine Greym-

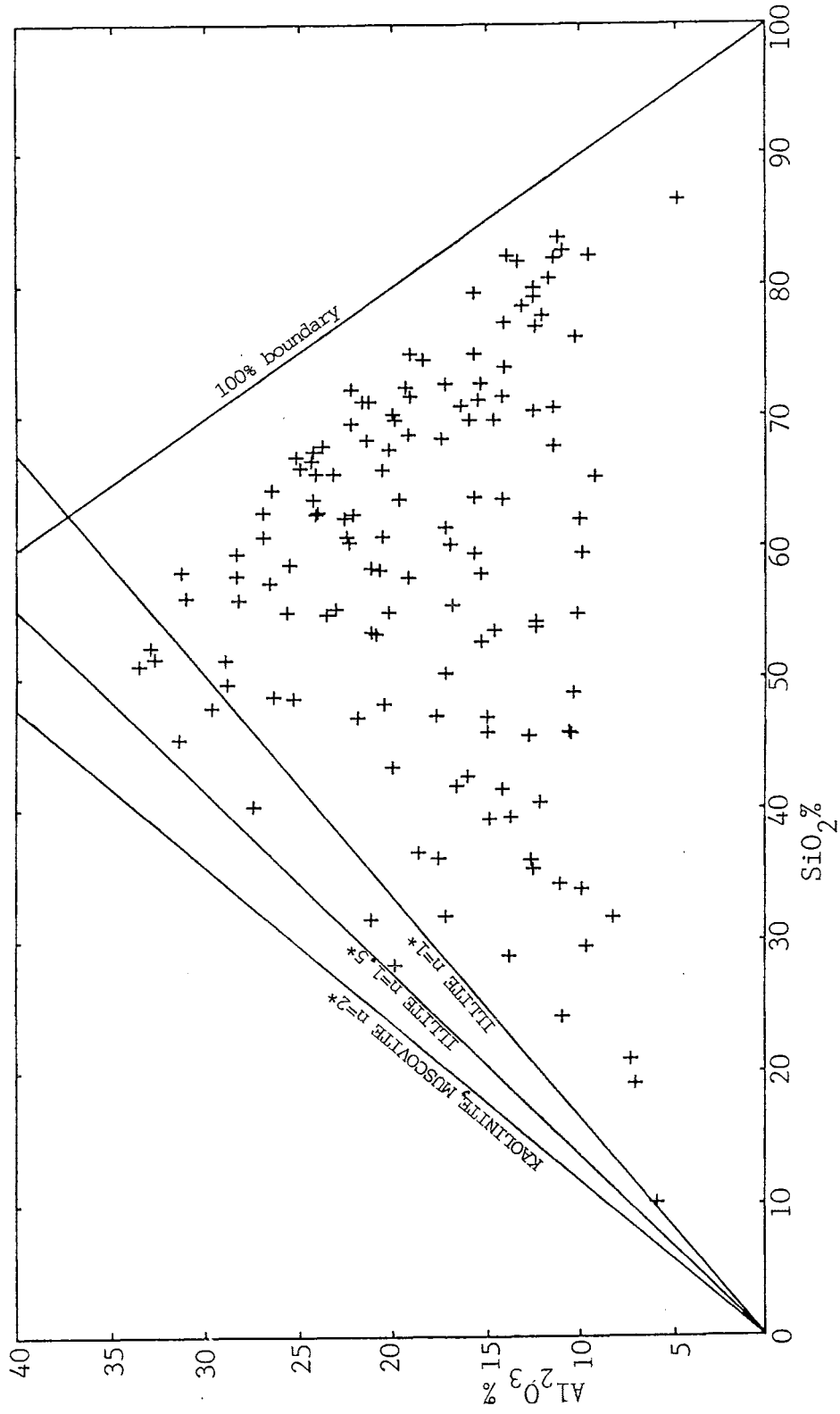


Figure 5.5 Plot of Al_2O_3 vs SiO_2 for all Greymouth Rewanui Member drillhole samples. *for description of illite composition see Section 2.6.2.

outh Paparoa coals by Budge and MacKnight (1976) show an average organic sulphur content of 0.35% (air dried basis). In 6 of these coals, neither sulphate nor pyritic sulphur could be detected; of the remainder, sulphide + sulphate sulphur ranged from 0.01% to 0.29%, representing 1.4% and 44% of the total sulphur, respectively. Some of the higher-sulphur composites from the Greymouth drillholes were analysed for forms of sulphur, and most of these results are listed in Table 5.3. Organic sulphur for this set of samples averages near 0.45%, whereas the average for total sulphur (excluding washed samples) exceeds 1.2%.

A value of 0.4% appears to be a best estimate for organic sulphur in Paparoa coal, where no forms of sulphur measurements are available. This assumption permits pyrite + marcasite estimation if sulphates can be ignored, i.e.

$$\text{sulphides in coal} = (\text{total S} - 0.4\%) \times 1.9 \ .$$

In the absence of pyritic sulphur determinations, use of this formula is preferable to assigning all iron to either sulphides or carbonate. Calculation of sulphide by this method should include a check to ensure that pyritic iron (calculated) does not exceed total iron. Examples listed in Table 5.3 suggest that this situation is unlikely to occur for the

Sample	Total sulphur %	Organic sulphur %	Source	Pyrite in coal, calculated from: total S[1]	total Fe[2]	inorganic sulphur[3]
DH 619						
26/060	0.70	0.33	(a)	0.57	1.58	0.70
26/067	0.69	0.22	(a)	0.55	2.23	0.89
DH 621						
26/133	0.82	0.32	(b)	0.80	1.68	0.95
DH622						
26/186	0.69	0.38	(b)	0.55	2.54	0.59
DH 635						
26/695 (washed)	0.98	0.62	(b)	1.10	4.26	0.68
26/695 (raw)	0.94	0.34	(c)	1.03	3.51	1.14
DH 641						
29/213	1.34	0.46	(c)	1.79	(no analysis)	1.67
DH647						
29/711	1.74	0.84	(a)	2.55	2.58	1.71
29/711	1.74	0.36	(c)	2.55	2.58	2.62
DH 650						
29/245 (washed)	1.28	0.46	(b)	1.67	2.75	1.56
29/245 (raw)	2.86	0.59	(c)	4.67	(no analysis)	4.31

Source: (a) CRA analyses, a.d. basis
(b) ACIRL analyses, d.a.f. basis
(c) This work, a.d. basis.
Total S from CRA analyses

Notes: (1) Calculated from (S-0.4)x1.9
(2) " " (Fe,0,xA/100)x1.5
(3) " " [S-S(org)]x1.9

Table 5.3 Relationship between total sulphur and pyritic sulphur for Rapahoe Sector Paparoa coals.

Paparoa data. The method should be applied with caution in the case of coals from the Dunollie Member and from Pike River, because of the absence of forms of sulphur data for these coals.

Siderite. Except for the occurrence of sulphide minerals in restricted areas of the Greymouth Coalfield (Chapter 6), siderite is considered to represent the only significant source of iron in the Paparoa coals. Manganese, magnesium, and calcium all show some degree of positive correlation with Fe_2O_3, indicating either substitution of iron in siderite, or some close association between carbonate phases, possibly due to alteration reactions. Some nodular siderite definitely contains mixtures of other carbonate minerals, and the observed correlations may be the result of a combination of lattice substitution and intimate mixtures, at least for CaO and MgO.

The $MnO-Fe_2O_3$ relationship (Figure 5.6) is well defined, and shows a linear regression of slope +0.75% MnO/100% Fe_2O_3. A similar relationship (0.8%) is shown by the density fractions for Strongman coal (Figure 5.2), except for the lightest floats where MnO declines relative to Fe_2O_3. This relationship is considered to be good evidence for incorporating all MnO in calculated siderite.

For MgO (Figure 5.7), and CaO (Figure 5.8), a positive correlation with Fe_2O_3 can be recognised, but the points are more scattered. This scatter is to be expected, in view of the number of different host minerals present (siderite, calcite, dolomite, crandallite). The position is further complicated by some occurrence of ferroan dolomite, although this is regarded as sufficiently rare to be neglected in mineral calculations.

In view of the complete solid solution which exists between $MgCO_3$ and $FeCO_3$ (Deer et al., 1962), and the very sparse occurrence of dolomite in Paparoa coals, all MgO has been calculated as part of total siderite. This assumption is also supported by good correlation between MgO and Fe_2O_3 in the sink-float fractions for samples 37/016 and P30 (Figures 5.2, 5.3). A somewhat arbitrary value of 1 CaO:10 FeO has been chosen to estimate the CaO occurring in siderite. This relationship plots mid-field in Figure 5.8, and approximates the relationship indicated by

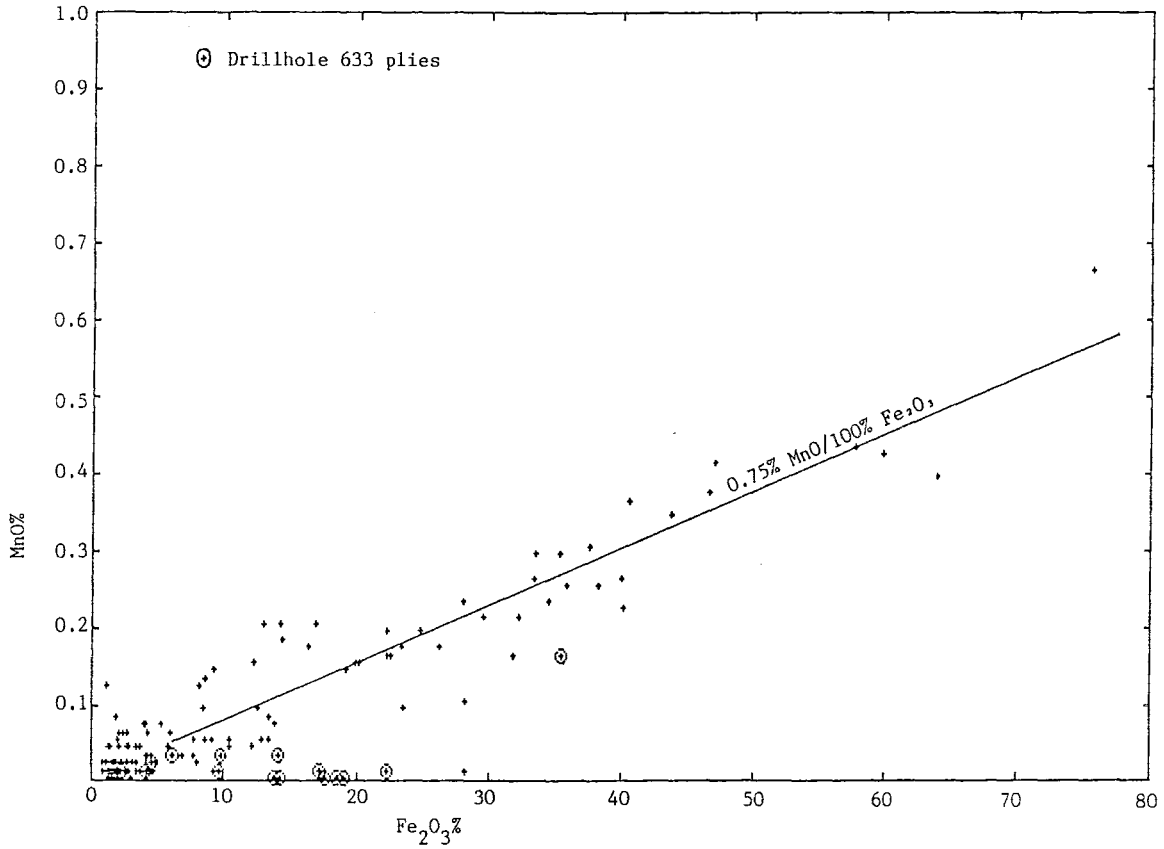


Figure 5.6 MnO vs Fe_2O_3 for Paparoa coals, Rapahoe Sector drillcore samples.

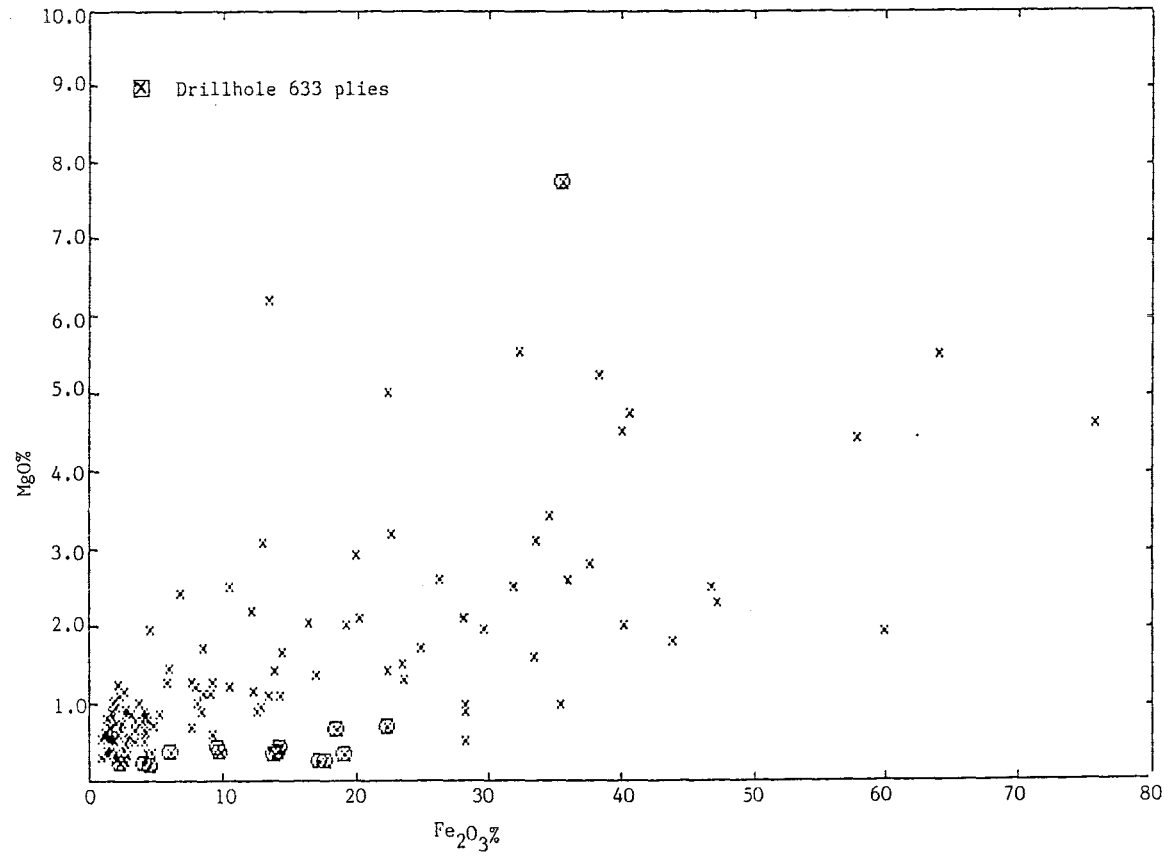


Figure 5.7 MgO vs Fe_2O_3 for Paparoa coals, Rapahoe Sector drillcore samples.

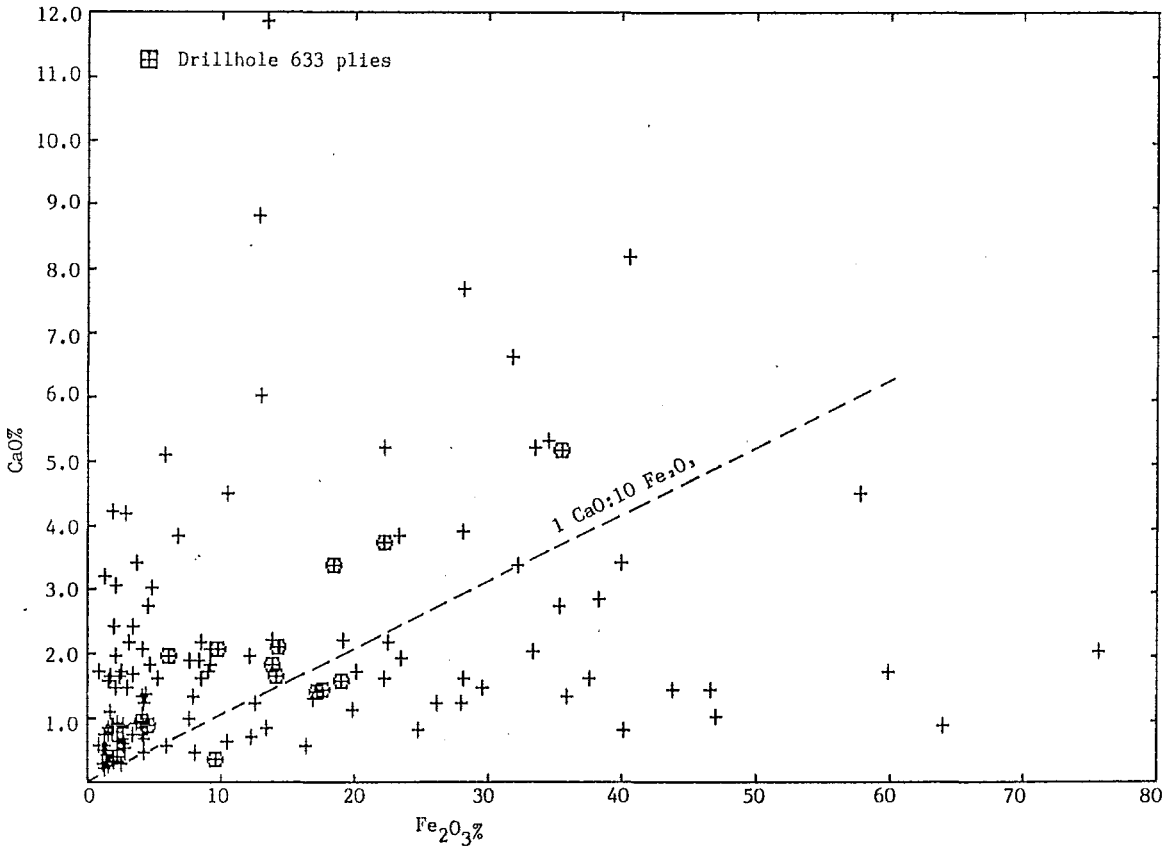


Figure 5.8 CaO vs Fe_2O_3 for Paparoa coals, Rapahoe Sector drillcore samples.

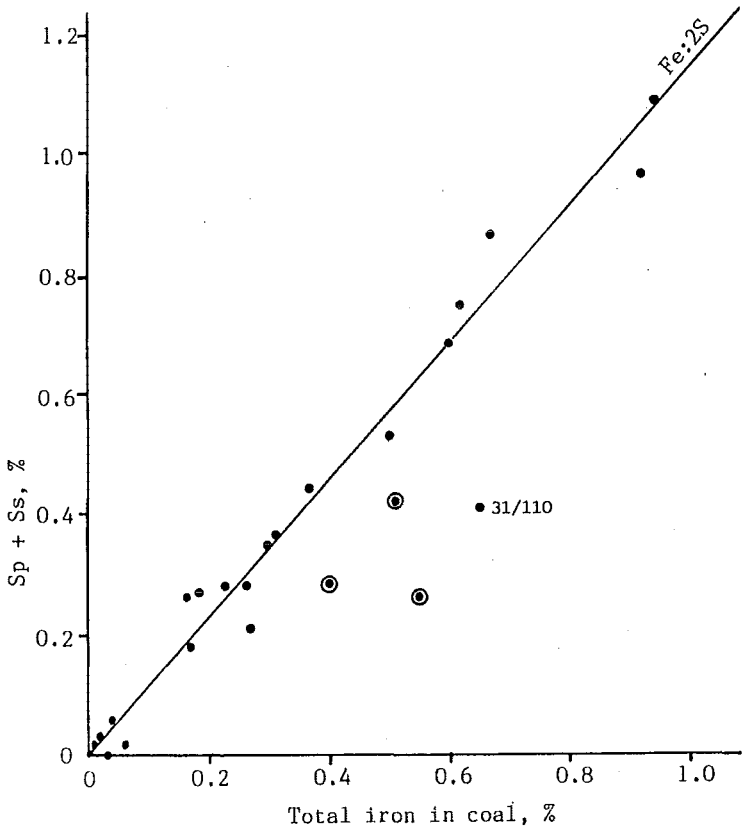


Figure 5.9 Pyritic and sulphate sulphur plotted against total iron, all expressed on a whole coal basis. Webb/Baynes samples, Buller Coalfield. circled points >7% ash 31/110 is highly weathered

drillhole 633 plies. Substitution by CaO to this extent corresponds to a typical "low Ca" siderite observed in non-marine coalmeasures by Matsumoto and Iijima (1981).

Chlorite. This mineral must be classed as extremely rare in Paparoa coal. An occurrence in the Pike River Coals appears to be restricted to unusual, boehmite-bearing seams. At Greymouth, the Strongman Mine coal also contains traces of chlorite, although this appears to be restricted to the -2μm fraction.

The occurrence of some chloritic interlayers within complex illite, however, must also be considered. Pankhurst et al. (1986) considered that some chloritic iron was present in sample P14, which contains abundant mixed-layer clay. Such an occurrence may explain the unusual trend of Fe_2O_3 in the light fractions of the washed sample 27/531, where iron sharply increases in the lightest fraction (Figure 5.1). The light float fractions of 27/531 have mineralogical and chemical affinities with the known chlorite-bearing coal (P33).

5.4.2 Brunner coals

Iron-bearing carbonates are absent from Brunner coals, with the exception of ankerite in the Flat Creek seam, and possibly traces of siderite in concretions at Garvey Creek. XRD shows the dolomite in Brunner coal to be low in iron.

Petrography and XRD suggest that iron sulphides (marcasite and pyrite) overwhelmingly dominate the mineralogy of iron in Brunner coals. Proper assessment of this observation requires chemical analysis; quantitative XRD would be greatly affected by the rapid oxidation of sulphide in coal samples, and possibly by further oxidation during or after low temperature ashing. Few Brunner samples have been analysed for both ash constituents and forms of sulphur. However, CRA carried out these analyses for 25 Webb-Baynes composites (Buller Coalfield), permitting a comparison between total iron and pyritic iron. Sheat (1984) plotted pyritic sulphur against iron for these samples and demonstrated a positive correlation, for which the regression line fell below the stoichiometric FeS_2 composition. Sheat used the observed relationship as an indica-

tor of pyritic/organic sulphur proportions but did not comment on the mineralogical implications.

When Sheat's data are replotted using a [pyritic + sulphate] sulphur axis instead of pyritic sulphur alone, good agreement with the FeS_2 relationship is exhibited (Figure 5.9), indicating that pyrite and marcasite are commonly the only significant iron minerals in unoxidised Webb-Baynes coals. However, some compositions still plot well below the pyrite line after correction for sulphate sulphur. Four of the worst fallout points are identified in Figure 5.9; all are uppermost composites, but only one is obviously weathered, as indicated by a high moisture value. This sample shows abundant weathering cracks in polished section, and also contains iron oxides occurring as pseudomorphs after pyrite and as fracture infillings (31/110, Figure 3.9). The other three samples are high ash coals (7.7, 21.4, 31.4% A), and may contain significant amounts of iron in silicates; at least two of these samples (31/088, and 31/052) are known to contain chlorite.

Some iron in Brunner coals occurs in chlorite and illite, as confirmed by Mössbauer work by Pankhurst et al. (1986). Unfortunately, no quantitative estimation of silicate iron could be obtained from the Mössbauer analyses. High-ash, illite-rich mineral matter from Brunner coal samples contains very little Fe_2O_3 (Table 5.4). Even if no allowance is made for pyritic iron, which will be present to some extent in all of these coals, the Fe_2O_3 content of illite in sample B26, for example, is no greater than 0.16% (dry basis) unless the percentage of illite present has been grossly overestimated. Furthermore, some of the iron in samples B13 and B27S can be expected to be present in chlorite. However, the composition of these minerals, separated from high-ash coals, may not be directly applicable to low-ash samples.

Table 5.4 Summary table of 6 "illitic" ashes from Brunner coals. See Table 4.3 for sample descriptions.

Sample	A%ad	MgO	Na2O	SiO2	Al2O3	SO3	P2O5	Fe2O3	MnO	TiO2	CaO	K2O	I%*	
B 8	16.7	0.87	0.22	47.87	37.53	0.29	0.21	1.58	0.02	7.81	0.55	4.69	49.1	
B 13	28.4	2.04	0.27	44.22	46.57	0.17	0.20	0.78	0.04	3.04	0.31	2.65	27.8	§
B 26	61.6	0.87	0.05	50.12	36.86	0.00	0.14	1.31	0.01	1.39	0.03	8.13	85.7	
B27S	45.2	0.63	0.11	43.89	45.81	0.18	0.20	2.31	0.00	1.60	0.22	3.77	40.0	§¶
B27F	6.0	0.43	0.30	34.11	52.88	1.68	0.38	1.18	0.00	3.73	1.64	2.60	27.4	
B28	0.2	0.94	4.58	52.59	19.35	4.44	0.05	2.81	0.04	3.12	5.00	1.12	13.5	

* calculated illite in total mineral matter ¶ pyrite identified § chlorite identified.

Because chlorite is sparse, no estimation of composition from bulk ash analysis is possible. Pankhurst et al. (1986) identified chloritic iron in a Greymouth Brunner coal (B3), but failed to detect this component in a Buller sample (B25) in which chlorite was known from XRD identification. This failure was probably a result of the very low mineral matter content of the Buller sample (0.5% ash).

It has not been possible to identify a mode of occurrence for manganese in Brunner coals. Levels of MnO in Brunner ash are extremely low, typically one tenth of Paparoa values. No satisfactory correlation with any other ash constituent, or total ash, is recognised. In the density fractions of Pike River Sample 30/121, MnO "washes out" with MgO, which suggests Mn substitution in dolomite.

5.5 MgO, CaO, P_2O_5, and Sr

5.5.1 Paparoa coals

The possible occurrence of MgO and CaO in siderite has been discussed. The overall weak correlation of these constituents with Fe_2O_3 suggests that MgO and CaO also occur in other minerals.

In general, MgO and CaO show a poor correlation (Figure 5.10), except within restricted sampling areas. Ply samples for DH 633 show a low and consistent ratio, with the exception of the magnesium and iron-rich ply 3. A continuous rise in both CaO and MgO in the lighter fractions of the sink-float sample 27/531 (Figure 5.1), combined with an identification of dolomite by XRD (Table 4.2), suggest that carbonate minerals may occur in some coals in finely divided form. This has not been confirmed by microscopy, and may be restricted to highly unusual coals. In contrast, MgO and CaO in the Strongman density fractions, where dolomite is also identified, "wash out" together as ash declines (Figure 5.2). However, in both samples 37/016 and P30, MgO shows a stronger correlation with Fe_2O_3 than with CaO.

Crandallite is an important source of calcium in Paparoa coals, and is probably the cause of many, but not all, of the anomalously high

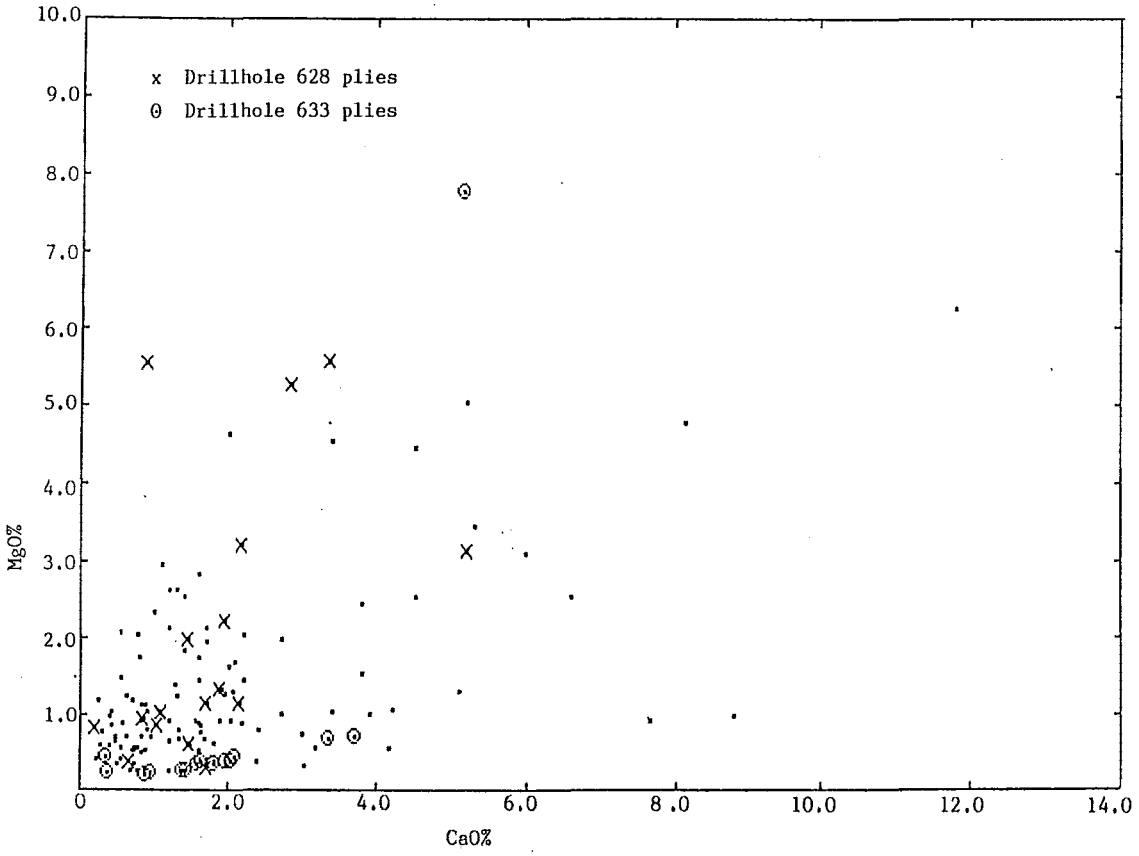


Figure 5.10 MgO vs CaO for Paparoa coals, Rapahoe Sector drillcore samples.

CaO/Fe_2O_3 and CaO/MgO ratios shown by some points on Figures 5.8 and 5.10. A comparison of XRD and chemical data indicates that crandallite abundance can be correlated with the following ash characteristics:

(i) high P_2O_5;
(ii) high strontium;
(iii) low SO_3/CaO ratios, and to a lesser extent,
(iv) high TiO_2.

The relationship between P_2O_5 and strontium in known and suspected crandallite-bearing coals is demonstrated in Table 5.5, where the maximum possible substitution of calcium is estimated. Barium determination for a small range of coals (Table 5.6) permits some indication of the extent to which this element might occur in the crandallite lattice. It is clear that the Paparoa crandallite is predominantly calcian. A proportion of the strontium and barium can be expected to occur in calcium carbonate minerals, as illustrated by strontium/CaO and strontium/P_2O_5 graphs (Figures 5.11 - 5.16), where some low-phosphate samples exhibit a very high Sr/CaO ratio. The DH 633 plies which show uniform

CaO/MgO also display a well defined positive correlation for Sr/CaO (Figure 5.15), suggesting the presence of calcite of relatively uniform composition throughout the seam.

The correlation between crandallite and low SO_3 in ash is a natural consequence of sulphation of carbonate CaO on combustion. This relationship is best shown by the ash from the Greymouth field samples, where phosphatic samples plot remotely from the other, more highly sulphated samples (Figure 5.17). The failure of some low-phosphate samples to plot near the stoichiometric $CaSO_4$ line can be attributed to the following possible causes:

(i) Depletion of total sulphur (where Ca + Na in whole coal is high).

(ii) Occurrence of Ca within coarse carbonate particles.

(iii) Some silicate-bound Ca.

Factors affecting the retention of sulphate in West Coast coal ashes are discussed elsewhere (Newman, N.A., 1987a; see also Appendix 3).

Petrographic and SEM evidence (Figure 3.11) suggest that crandallite occurs as very fine particles within the coal. This is consistent with the trend shown by the washed fractions of sample 27/531, where CaO, P_2O_5, and Sr all tend to increase in the lighter fractions (S.G. >1.24, Figure 5.1). However, while P_2O_5 and Sr decline sharply in the fraction F 1.24, CaO does not, indicating a change in mineralogy in the ultra-low ash coal. A similar trend for CaO and P_2O_5 can be seen for the Strongman Mine fractions (Figure 5.2).

5.5.2 Brunner coals

Calcite and dolomite are widespread in Brunner coals, although these minerals occur very sporadically, except in the Pike River Brunner seam where they are abundant. The mixture of these two carbonates, with dolomite dominant, is well illustrated by the CaO/MgO relationships for Pike River samples (Figure 5.18). However, the sink-float fractions for a Pike River Brunner coal (30/121, Table 5.2) show that CaO does not follow MgO in "washing out" as ash declines. CaO remains abundant in the light fractions, either as ultra-fine calcite, or in organic combination.

Sample	Ash constituents, % P_2O_5	CaO	SrO	CaO/P_2O_5	CaO equivalent of [CaO + SrO]	CaO equivalent required by P_2O_5 for Crandallite	Maximum possible substitution of Ca by Sr, in Crandallite Mole%
P3	0.65	0.78	0.164	1.20	0.78	0.25	35%
P9*	0.82	0.45	0.128	0.55	0.52	0.32	22%
P10	4.55	2.90	0.627	0.64	3.24	1.77	19%
P13*	6.21	2.65	1.317	0.42	3.36	2.42	29%°
P21*	3.02	1.36	0.116	0.42	1.42	1.18	5%
P28	1.91	1.06	0.576	0.55	1.37	0.75	42%
26/362*	4.20	1.71	0.480	0.41	1.97	1.63	16%
26/363*	3.05	5.19	0.143	1.70	5.27	1.19	6%

*Crandallite detected by XRD °a further 6% substitution by Ba is possible

Table 5.5 Comparison of P_2O_5, CaO, and SrO in ash for some Greymouth Paparoa coals.

Sample	A%a.d.	Ba(ppm) in ash	CaO equivalent, % in ash	Sr(ppm), in ash	CaO equivalent % in ash	P_2O_5 % in ash	CaO % in ash
P4	2.1	3638	0.118	1131	0.072	1.01	1.22
P13	0.4	4688	0.152	11137	0.711	6.21	2.65
P20	3.8	1162	0.038	281	0.018	0.17	0.17
P28	19.2	1001	0.032	4868	0.311	1.91	1.06
P34	18.4	749	0.024	1207	0.077	0.47	0.61
P35	13.0	1481	0.048	1902	0.121	0.79	0.79

Table 5.6 Barium concentrations in some Greymouth Paparoa coals, computed as Ba in ash, and compared with concentrations of CaO, Sr, and P_2O_5.

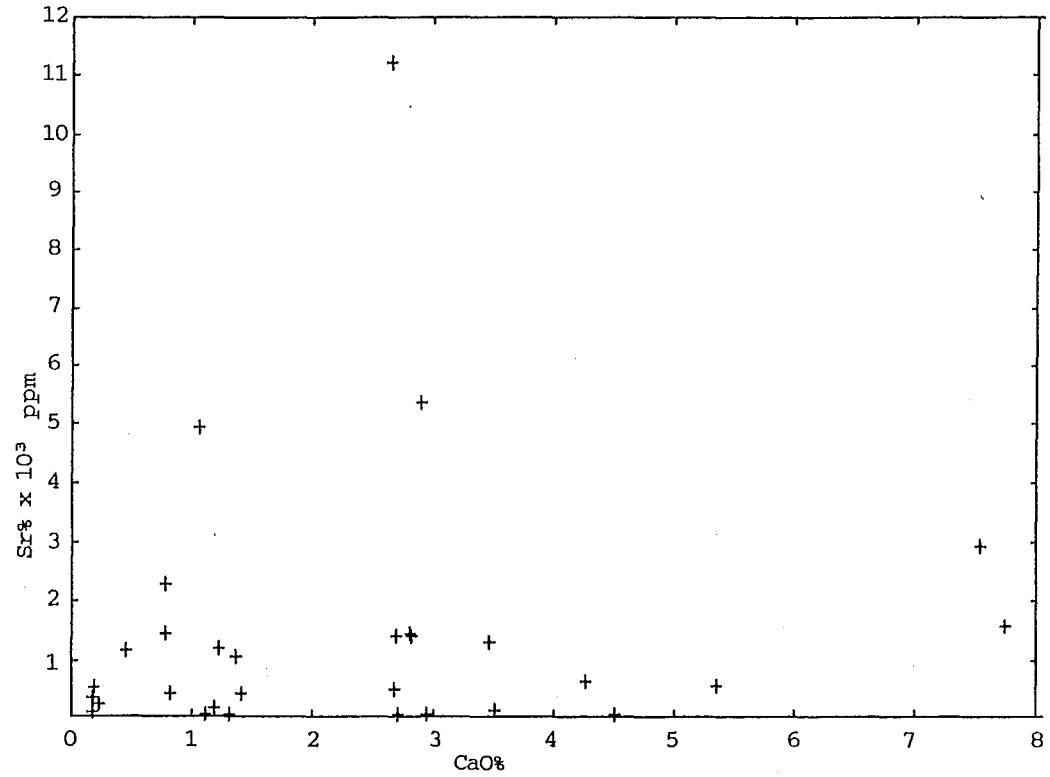


Figure 5.11 Sr vs CaO in ash for Paparoa coals; Greymouth field samples. High Sr samples contain crandallite.

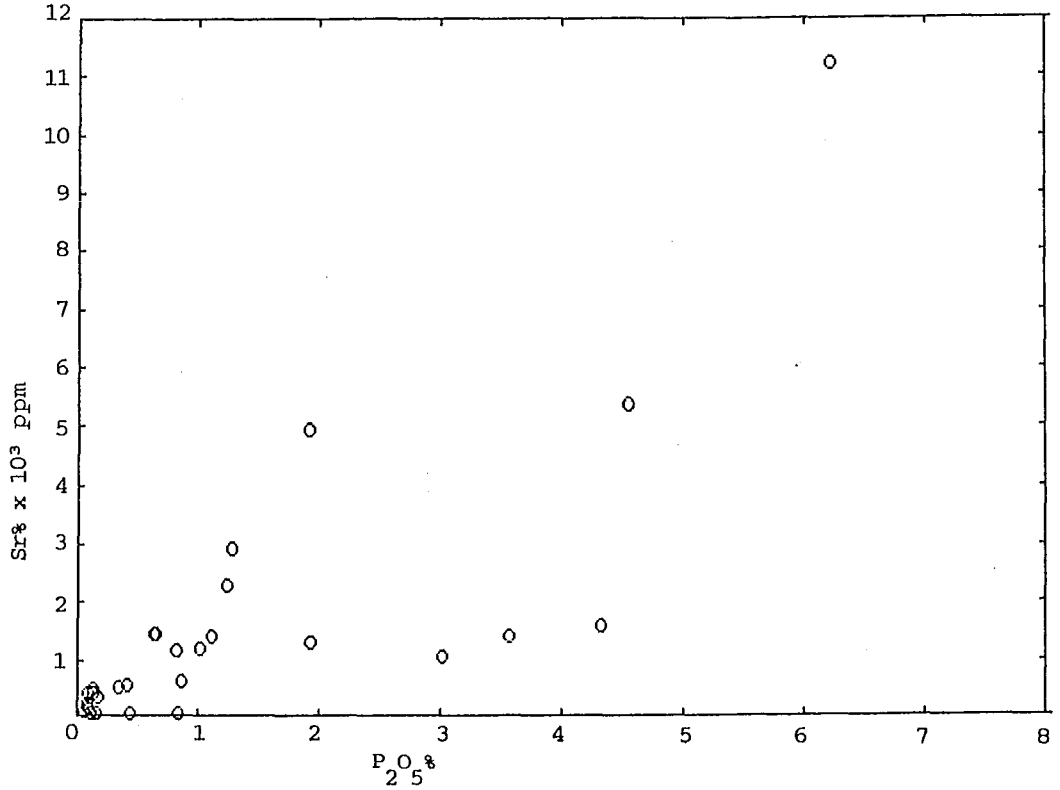


Figure 5.12 Sr vs P_2O_5 in ash for Paparoa coals; Greymouth field samples.

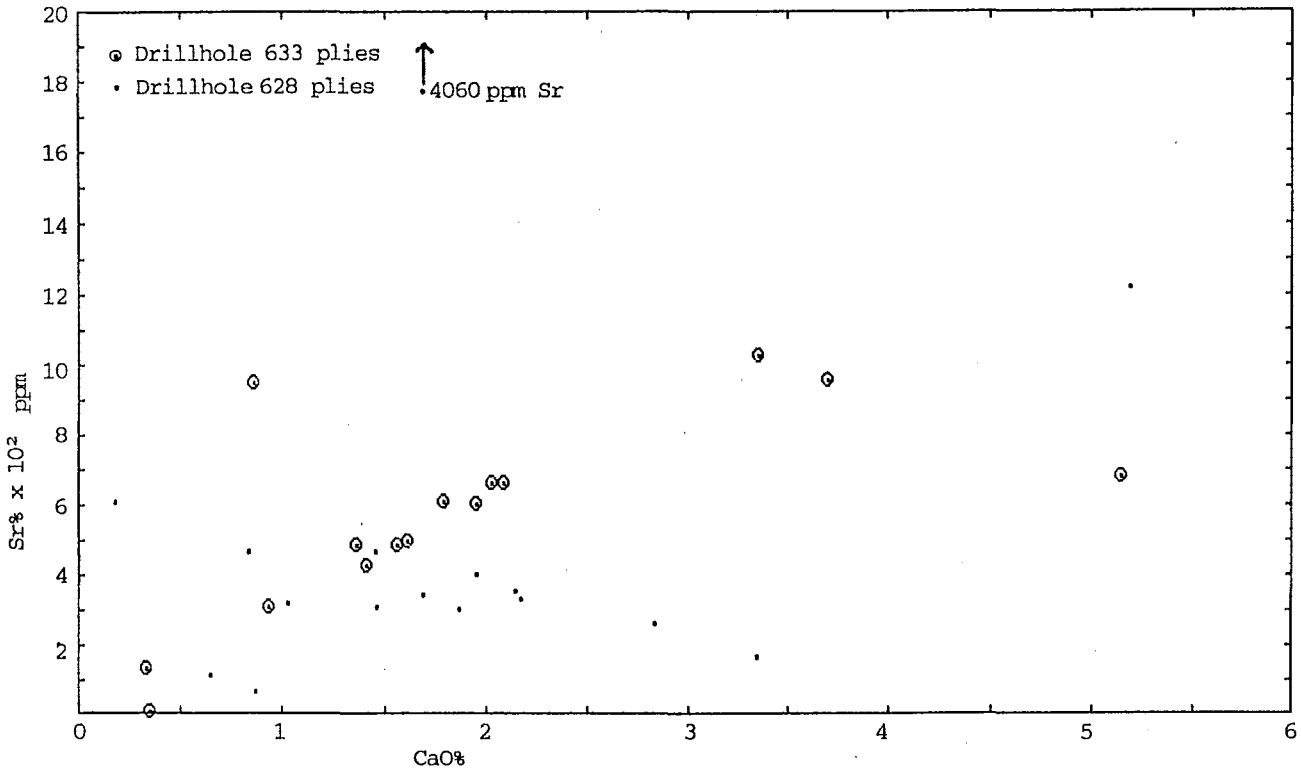


Figure 5.13 Sr vs CaO in ash for Paparoa coals; plies from 2 thick seams in the Rewanui Member. The seam in Drillhole 628 contains crandallite, whereas the other seam does not.

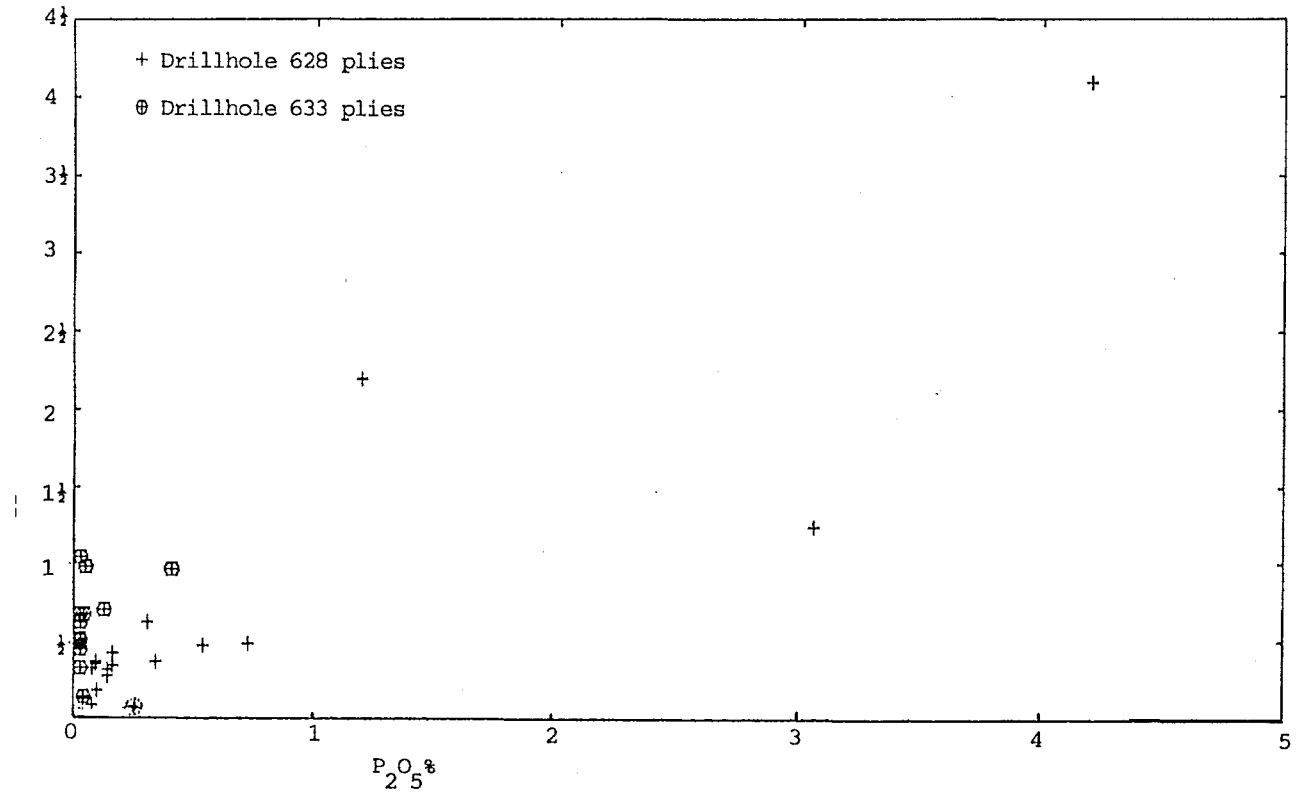


Figure 5.14 Sr vs P_2O_5 in ash for Paparoa coals; plies from 2 thick seams in the Rewanui Member.

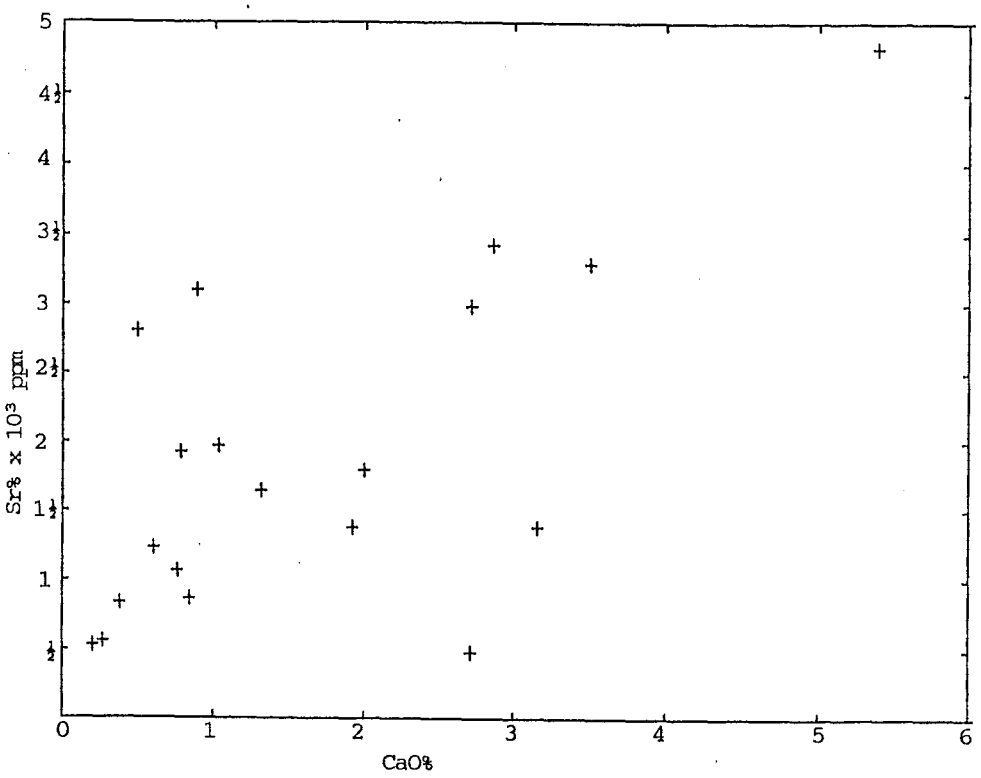


Figure 5.15 Sr vs CaO in ash for Paparoa coals; field samples from Pike River Coalfield.

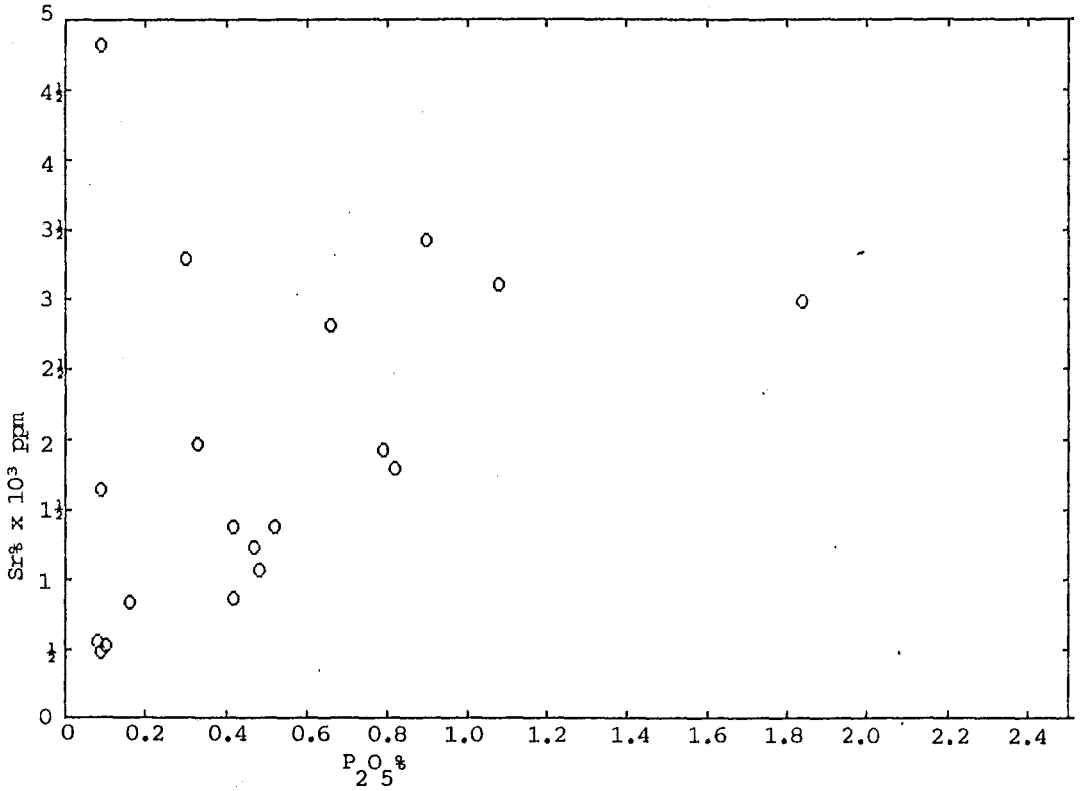


Figure 5.16 Sr vs P_2O_5 in ash for Paparoa coals; field samples from Pike River Coalfield. Many samples are known to contain crandallite.

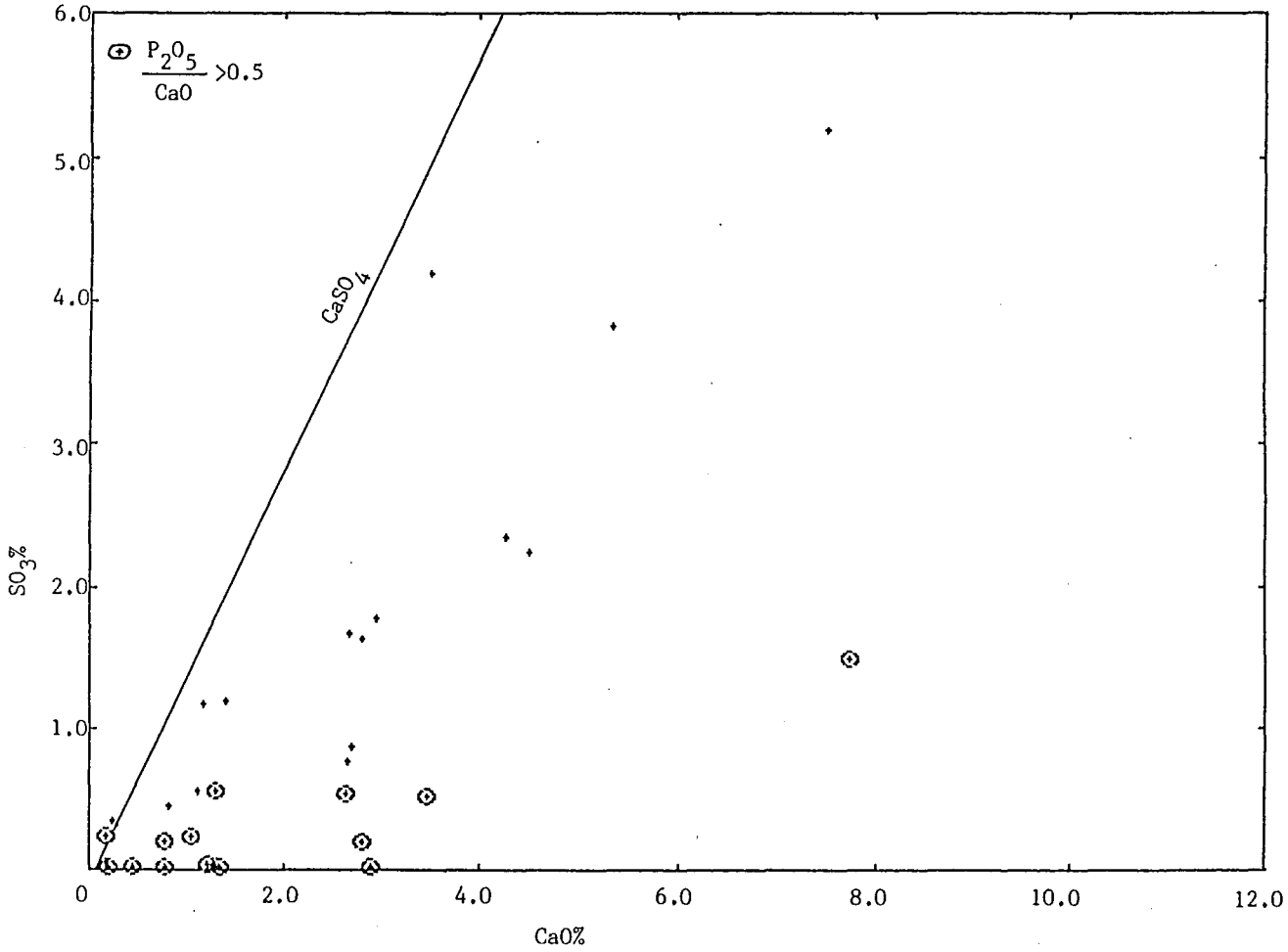


Figure 5.17 SO_3 vs CaO (as ash constituents) for Greymouth field samples, Paparoa coals.

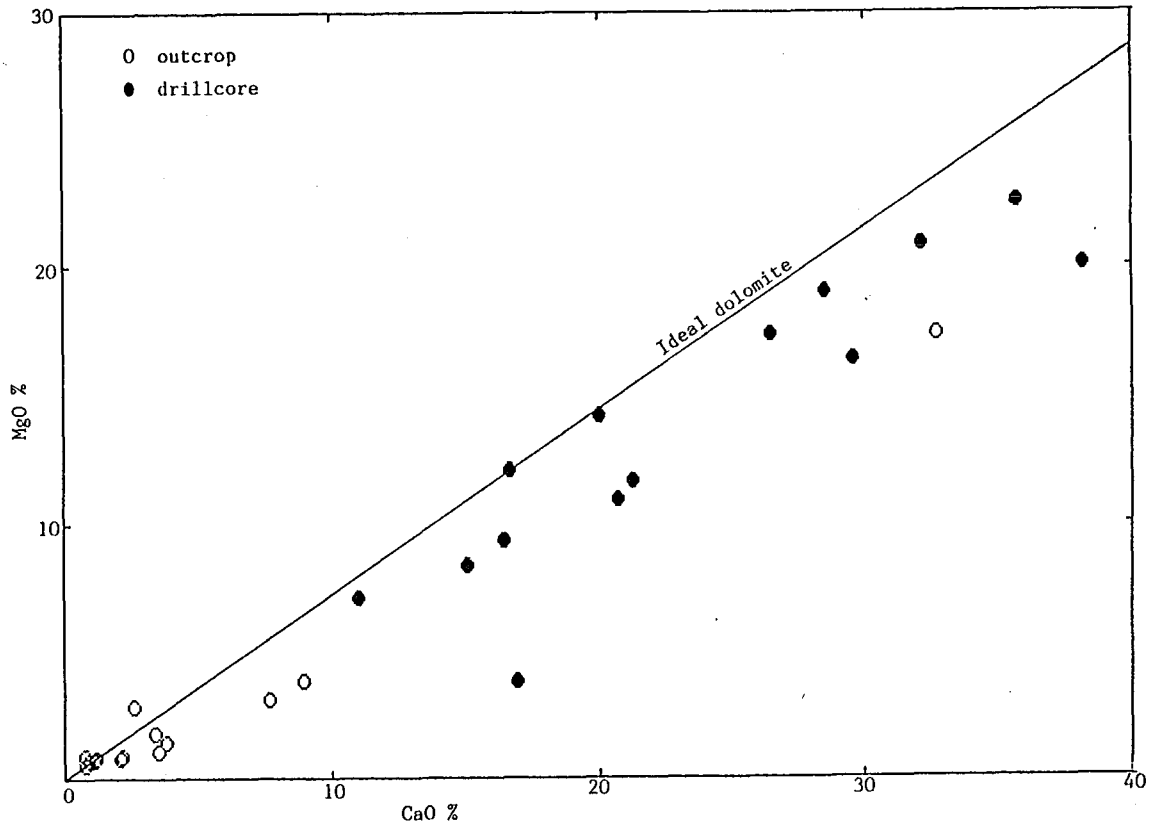


Figure 5.18 MgO vs CaO for Pike River Brunner coals.

In the Greymouth Brunner sample B14, an excellent correlation between CaO and MgO is consistent with dolomite identifications by XRD. Although both oxides rise as ash declines, suggesting organic combination, the presence of carbonates in the lightest fraction (F 1.3) is confirmed by XRD, indicating an intimate dispersion of fine-grained minerals in the coal. The excess MgO over dolomite composition may occur as chlorite, which is known to be present in this coal. Similarly, chlorite is probably a significant host to magnesium in coals within parts of the Buller Coalfield. Analyses of the more highly illitic Brunner ashes in Table 5.4 suggest that illite in these coals may contain approximately 1% MgO. Some of this may be present as discrete chlorite, or possibly as chlorite interlayers.

Crandallite is known to occur sporadically throughout the Brunner coals, but correlations of P_2O_5 with CaO and Sr are generally too greatly affected by carbonate minerals to show any clear relationship. However, most phosphate-rich Brunner ashes can be shown to correlate with crandallite identification by XRD of mineral matter. Strontium is not chiefly restricted to crandallite in Brunner coals; carbonate-bearing samples exhibit a wide variation in Sr/CaO ratio, which reaches an extreme value in a Greymouth sample (B20, Table 4.3), in which aragonite is present.

Strontium values were not available for coals analysed by CRA or ACIRL.

The foregoing discussion has dealt chiefly with bituminous coals. In the case of the few sub-bituminous coals included in this study, much of the inorganic material may occur organically bound. This applies particularly to calcium. A limited investigation by means of cation exchange analyses is discussed in Chapter 7.

5.6 TiO_2

Apart from XRD patterns there is no evidence concerning the mineralogy of TiO_2 in West Coast coals. Rutile has been confirmed in TiO_2-rich mineral matter, but other Ti species (e.g., anatase, brookite)

have been reported in coals overseas and may be present in the West Coast seams. Because the major peak for anatase is obscured by a strong 3.5Å peak for crandallite, some undetected anatase may be present, particularly in view of the observed correlation between high TiO_2 values and high P_2O_5 values.

Paparoa coals generally exhibit much higher TiO_2 in ash, and TiO_2/Al_2O_3 ratios than do the Brunner coals. In the density fractions of all the sink-float samples except B14 (Figures 5.1-5.4, Table 5.2), TiO_2 increases as ash declines. The sharp drop in TiO_2 in the lightest fraction for 27/531 indicates an organic association, rather than organic bonding. This behaviour shows that TiO_2 occurs in these coals in finely divided form, possibly in thin fibres as illustrated in Figure 3.11. Some TiO_2 may be present as small grains associated with fine grained kaolinite, in which TiO_2 is known to vary with surface area (Weaver and Pollard, 1973).

Unusually high phosphate values tend to correlate with the highest TiO_2 values (e.g., samples P13, P28, 27/156 and 26/362; Table A2.1, Appendix 2.), but the overall correlation between these two ash constituents is poor.

5.7 K_2O and Na_2O

Illite, as defined and described in Chapter 3, is considered to be the sole source of K_2O in unweathered West Coast bituminous coals. In the sink-float fractions, K_2O commonly declines with ash, and in every case, the K_2O/Al_2O_3 ratio declines with ash. These data show that K_2O in the coals is entirely associated with particulate mineral matter.

In contrast, occurrence of sodium in West Coast coals is more complex. For all the sink-float samples except B14, Na_2O increases as ash declines, demonstrating a strong organic association. Erratic fluctuation in Na_2O content for the B14 ashes can be attributed to the presence of dawsonite, which is a major host to sodium in Greymouth Brunner coals, and to some extent, low-ash plies at Buller Coalfield.

Some dawsonite also occurs in Paparoa coal (27/531), but appears to be restricted to unusual seams of hyperaluminous character. In other Paparoa coals, the highest sodium values correlate with an unusual illite, which exhibited the following characteristics:

(i) A broad and sometimes complex 10Å peak, often with both high and low-angle "tails" superimposed on a sharper central peak (e.g., P14, Figure 3.4).
(ii) Some degree of expansion on glycollation. No peaks developed in the 16 - 18Å region, as would be expected from significant smectite interlayering, but the 10Å low-angle tail flattened and extended, and the baseline below 17Å became elevated.
(iii) Separate peaks resolved at 3.33 and 3.21Å (air dried), assumed to represent illite 003 and smectite 005, respectively.
(iv) Some examples showed a baseline shoulder below 20Å, both before and after glycollation, suggesting some short-range, regular ordering of interlayers.
(v) In some cases, failure to collapse on heating to 350°C, suggesting the presence of hydroxyl-Al or -Mg interlayers (Jackson, 1963).

Examples of coals which produce mineral matter of this type are listed as Group a, Table 5.7, where the discrepancy between measured and calculated total illite can be seen to sharply increase with sodium content. The table also shows that sodium in ash is grossly undersaturated with respect to sulphate, which strongly suggests that most of the sodium occurs within silicate minerals.

Assignment of sodium to silicates in these samples can be assessed in terms of the following possibilities:

(i) Sodium as ionic interlayer species within the smectite component of the mixed layer clay.
(ii) Sodium occurring in the mica layers of the mixed layer clay.
(iii) Sodium occurring in some silicate which cannot be detected by XRD, or which decomposes during preparation.

Table 5.7 Ash composition and mineral characteristics for sodium-rich Paparoa coals.

Sample	A%a.d.	% in ash Na_2O	% in ash K_2O	% in ash SO_3	Na_2O/K_2O	Illite XRD	Illite Calc.
Group a.							
P3	2.9	1.25	0.45	0	2.78	9	5
P4	2.1	1.91	0.47	0.02	4.06	19	6
P11	2.4	3.78	0.78	3.79*	4.85	37	17
P14	1.6	5.31	1.44	0.75	3.69	38	21
27/531 F1.26-S1.24)	2.4	4.03	1.27	6.75+	3.17	54	22
Group b.							
26/652	2.5	5.05	0.52	6.96	9.71	n.d.	
26/653	2.0	5.43	0.45	7.61	12.07	5	9
26/654	4.8	3.42	0.35	1.63	9.77	<3	4

* >5.0% non-crandallite CaO present
\+ >4.7% non-crandallite CaO present

Neither (i) nor (ii) are satisfactory explanations. If some allowance is made for quartz and kaolinite in these coals, it can be seen that insufficient smectite is present to account for all the sodium as interlayer cations, even using the most extreme of smectite compositions (Weaver and Pollard, 1973). Furthermore, if strongly sodic smectite were present, swelling properties far better than those observed would be expected. Additional sodium could be present in the form of paragonitic mica sheets, but the XRD patterns fail to show significant quantities of such material. Some combination of (i) and (ii) may be present, if the > 20Å shoulder can be interpreted as the presence of rectorite layers (Brown and Wier, 1963). The possibility of some unstable mineral phase decomposing or substantially altering during preparation must be acknowledged, but no direct evidence can be presented to support this.

Whereas the association of the illite characteristics outlined above with high-sodium ashes is consistent, the reverse situation is not. Plies 5-9 from DII 633 produce very sodium-rich ashes in which Na_2O/K_2O ranges to more than 10 (Group b, Table 5.7) yet only traces of illite can be observed in the mineral matter, and the smectite character cannot be detected. The total illite fraction, although low, is correctly estimated by calculations based on potassium alone. Chemical analyses show the Na_2O content to be highly sulphated in ash, therefore, it is concluded

that sodium occurs in this coal in predominantly organic association.

The sink-float Paparoa sample from Pike River (27/531) represents a third variation of sodium occurrence, in which both "sodic smectite" characteristics and dawsonite are present. Washing trends for this unusual coal show a regular, curved slope for K_2O which consistently declines with ash, and apart from a minor inflection, a linear increase in Na_2O as ash declines (Figure 5.1). The progressive reduction in slope for the K_2O trend can be attributed to both textural and compositional variation in illite. The heavy fractions can be expected to contain the coarse, potassium-rich illites, whereas the lighter coal will host a more finely divided variety which can be expected to contain less potassium in the mica layers and a higher proportion of smectite layers. The most finely divided clays can be expected to be the most smectite-rich, if the mineral matter conforms to trends observed in other geological materials (Gibbs, 1967).

In general, it appears unlikely that either dawsonite or organic association can account for a major fraction of sodium in Paparoa coals. A graph of sulphate against Na_2O (as ash constituents) for Greymouth drillhole samples (Figure 5.19) shows that a large proportion of these ashes contain unsulphated sodium. Because many of these samples represent low ash coals, and contain little competing CaO, it is difficult to envisage their sodium content occurring in any form other than a silicate mineral.

It must be emphasised that the coals described here are not sodium-rich in absolute terms; sodium-in-coal values are typically less than 0.1%. Figures 5.20 and 5.21 allow a comparison of the major West Coast coal deposits with respect to their sodium content. These graphs of Na_2O in ash against reciprocal of ash show the dominant, "organically-associated" trend of the points in each case, with the exception of the Pike River Brunner samples, for which the points are more scattered. The magnitude of Na_2O-in-coal is proportional to the slope of a radial line passing through the origin, as indicated in Figure 5.20. The one West Coast coal which can be distingiushed as sodium-rich in international terms is the Heaphy Mine product (Table 4.3), from which Na_2O in ash exceeding 10%, and more than 0.35% Na-in-coal, have been meas-

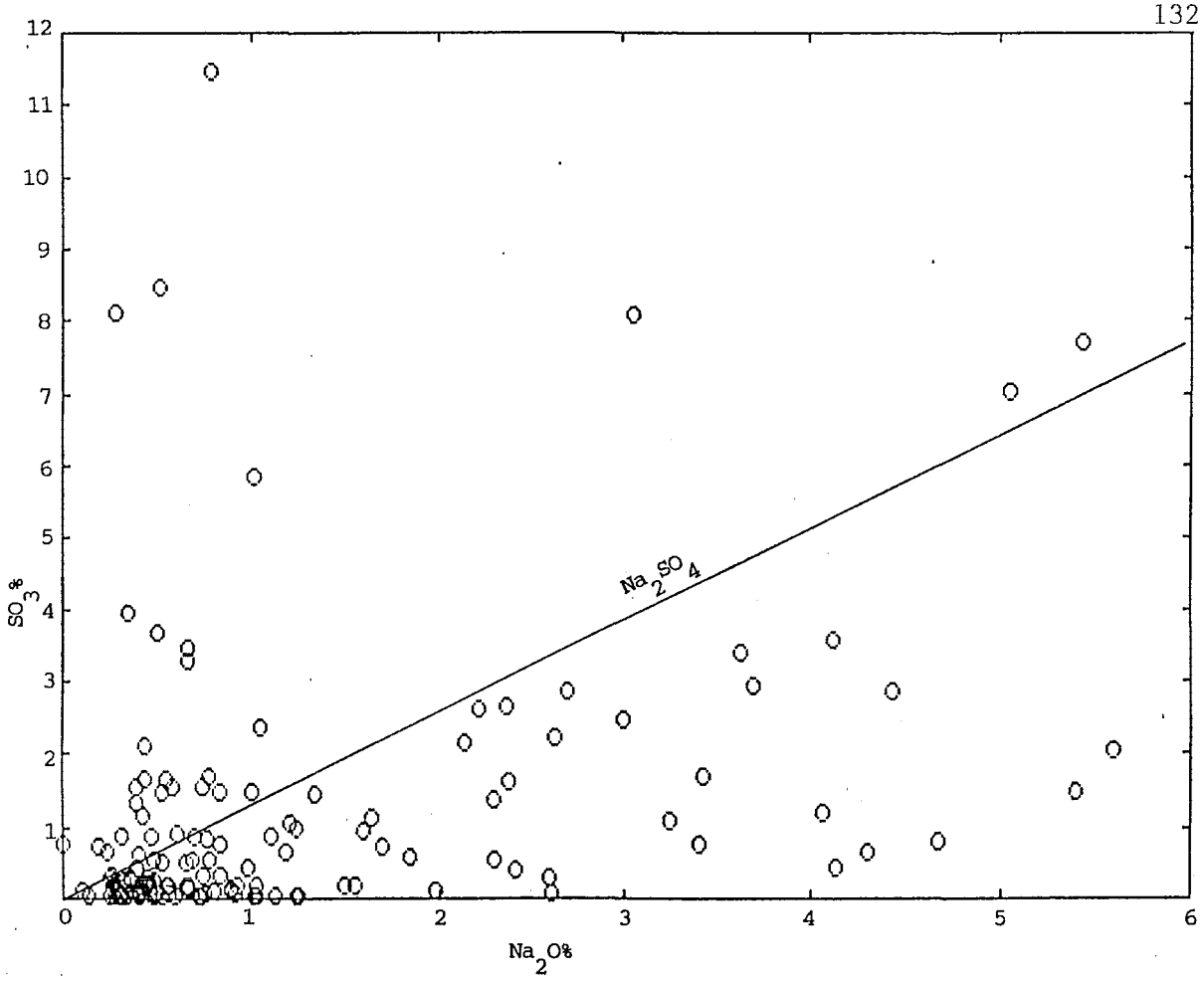


Figure 5.19 Na_2O vs SO_3 as ash constituents for all Rapahoe Sector drillcore samples. Samples above the Na_2SO_4 line contain high carbonate calcium.

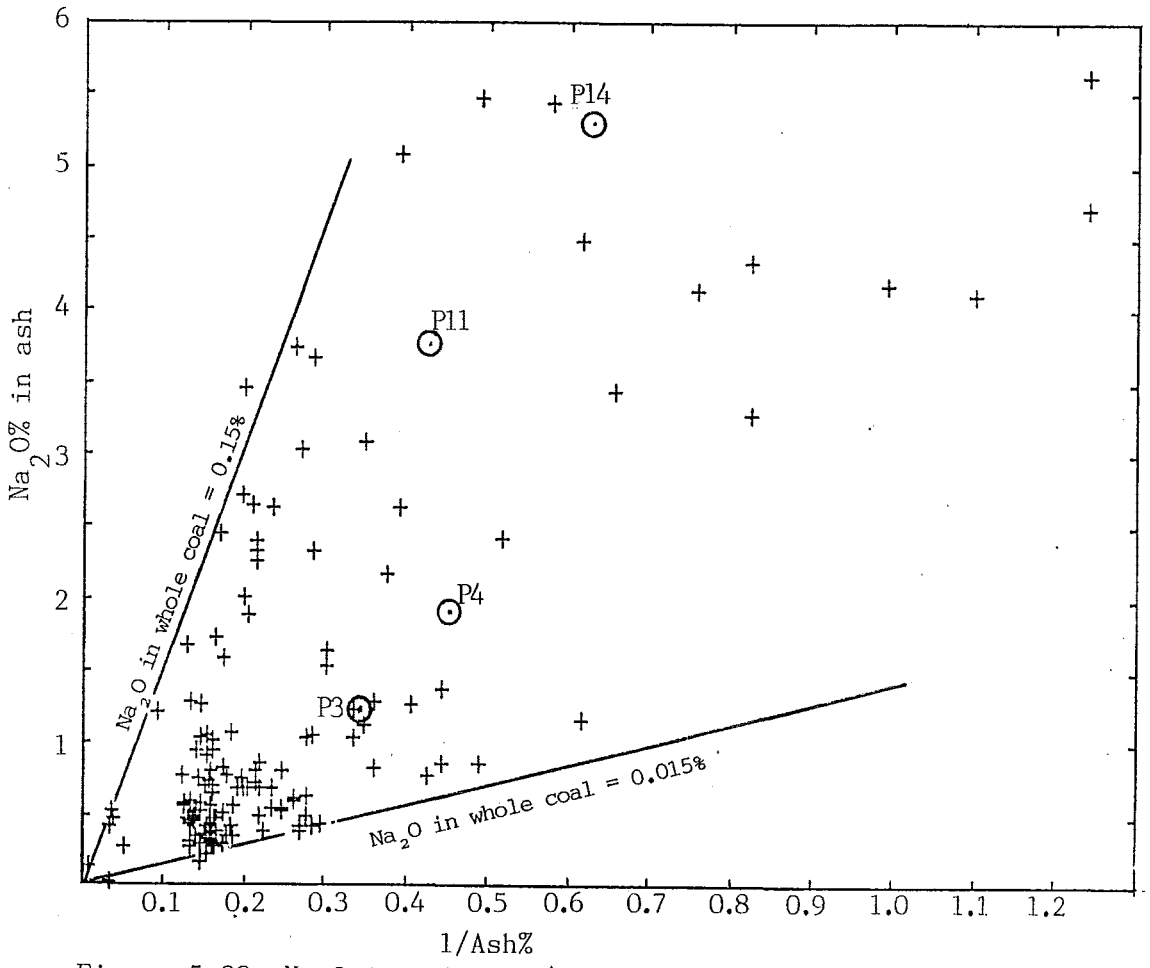


Figure 5.20 Na_2O in ash vs 1/Ash for Greymouth Paparoa coals. Crosses = Rapahoe Sector drillhole samples, circles = field samples described in Tables 4.2 and 5.7.

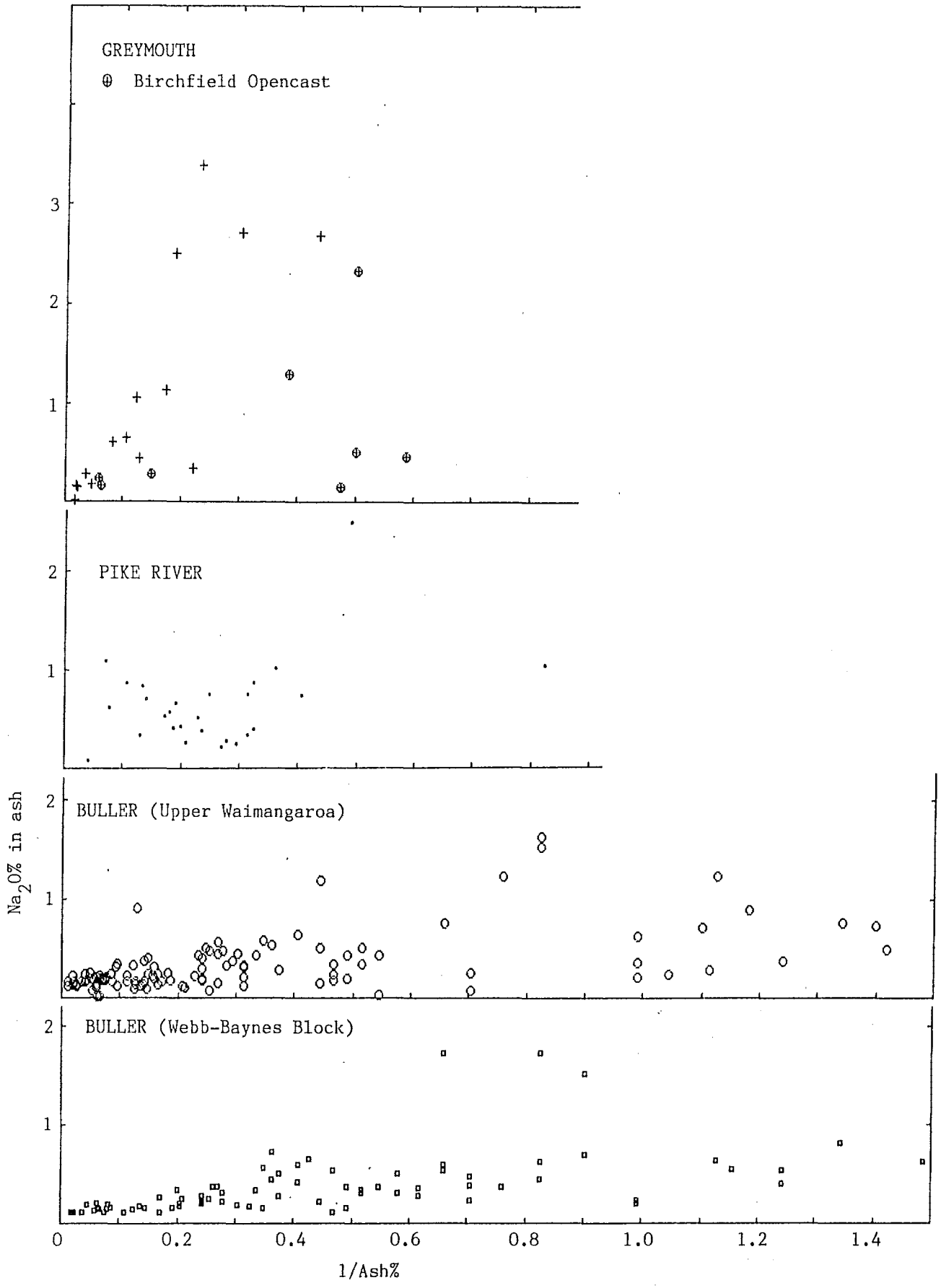


Figure 5.21 Na_2O vs 1/A for high rank Brunner coals.

ured (CRA records). No mineral source can be identified for this sodium, which is partly acetate-exchangeable (Chapter 7).

5.8 NICKEL

Nickel values for West Coast coals show a very large fluctuation, both in ash, and on a whole coal basis. Nickel values for sink-float fractions are available only in the case of the two Pike River coals, 27/531 and 30/121 (Figure 5.1 and Table 5.2). Density fractions for both of these coals show nickel concentrating in the floats. The Paparoa sample (27/531) shows a well-defined linear trend, which in the floats region corresponds to approximately 8.5 ppm Ni in "pure coal". The Brunner fractions (30/121) reflect a more erratic behaviour for this element, but indicate a Ni-in-coal value of around 3-4 ppm. These values are an order of magnitude lower than nickel in the Paparoa Coal Measures sediments (Chapter 6). However, it can be shown that sedimentary partings or high ash zones within the seams are commonly depleted in nickel, relative to the coal measure mudstones, and that the major authigenic minerals do not contribute significant nickel to the coal.

CHAPTER 6

CONTROLS ON MINERAL MATTER IN PAPAROA COALS

6.1 INTRODUCTION

The principal controls on the mineralogical and chemical composition of mineral matter in coal can be defined as follows:

(i) Composition of source material.

(ii) Environment of deposition.

(iii) Diagenesis during burial.

The composition of sediment entering a peat swamp can be expected to exert a major influence on the resulting mineral matter. The sedimentary input can be evaluated by examining interseam sediments and remnants of known source rocks, if exposed, but assumptions must be made concerning the size fraction incorporated as mineral matter in the coal, if useful comparisons are to be made.

The environment of deposition must be considered a potentially important factor controlling mineral matter composition, because this stage involves alteration and sorting of the sediment within the depositional basin, followed by a more extreme period of alteration when the sediment enters the swamp. The character of sediment transported into peat swamps is partly dependent on current energy, which is a major control on sediment texture. Generalised texture – composition relationships are shown in Figure 6.1, which demonstrates the increase in quartz and mica flakes at the expense of clay as particle size increases from clay to sand. These relationships, however, may not be directly applicable to the depositional environment of the Paparoa Coal Measures, where rock fragments and feldspar may have been relatively abundant in the fines, because the effects of chemical weathering were reduced by proximity to, and rapid uplift of, surrounding source rocks. After deposition, swamp characteristics such as pH, water table level, and degree of drainage, are all believed to influence mineral matter by controlling the type and rate of chemical alteration of original minerals.

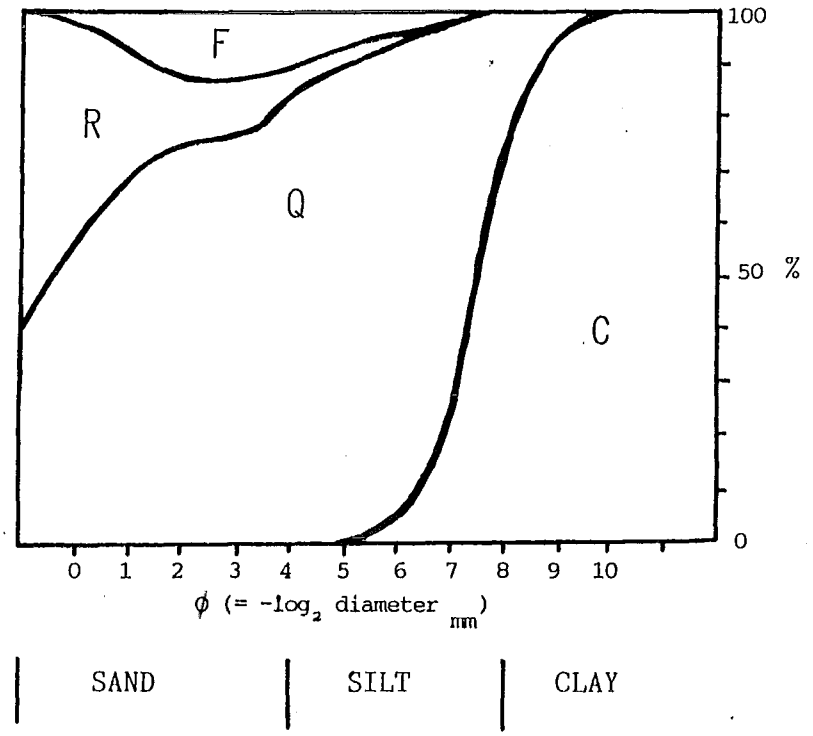


Figure 6.1 Typical texture-composition relationships exhibited by sediment from an average composition silicate rock source. Data from Blatt et al. (1972), Figure 8-19. C = clay minerals Q = quartz & mica flakes R = rock fragments F = feldspar

When burial removes mineral matter from the influence of the swamp surface, diagenetic reactions will continue at a rate determined by peat character and groundwater conditions. New minerals can be expected, initially as a result of rising pH, and subsequently in response to thermal effects and a change in the organic matrix as the peat to coal maturation proceeds.

6.2 SOURCE

6.2.1 Greenland Group

The Greenland Group is a thick sequence of lower Paleozoic greywackes and argillites (Laird, 1972) which underlies the Paparoa Coal Measures at both Greymouth and Pike River. Within the Greymouth Coalfield, early Paparoa sedimentation (Jay-Waiomo Members) deposited material from the Greenland Group and locally abundant volcanics, whereas later units (Rewanui-Dunollie) received mixed Greenland Group, granite, and contact metamorphic rocks from granite margins (Gage, 1952).

The petrology of the Greenland Group, as described by Laird (1972) and reviewed by Nathan (1976), shows that these rocks have uniformly quartz-rich composition. The greywackes contain 35-40% detrital quartz, and less than 6% sodic plagioclase and fine grained rock fragments, in a matrix of fine grained chlorite and sericite; alkali feldspar is absent. Nathan provides a detailed description of Greenland Group geochemistry, which includes a number of analyses for greywacke and argillite from several areas on the West Coast. Nathan's data for localities immediately north of Greymouth Coalfield have been averaged and included in Table 6.1.

6.2.2 "Morgan Volcanics"

To date, there is no established lithological name for the extrusive rocks which are locally abundant in the Morgan Member at Greymouth, and the probable lateral equivalent Paparoa Member 3 at Pike River. Gage (1952) distinguished the volcanic rocks as a separate facies of the Morgan Formation (now Member), although he was aware that tuffs were present outside this unit. Almost no petrological or geochemical work has previously been carried out on these rocks. Gage describes basalt and lamprophyre, rarely found as flows, but commonly present as clasts within thick conglomerates which have a tuffaceous matrix. Newman (1985a) reports rhyolite clasts in the Morgan Member in the northwest of Greymouth Coalfield.

Extensive pyroclastic deposits are found throughout much of the Waiomo Member, although their volumetric contribution is small (Figure 6.2). The ashfall horizons within the mudstone form distinctive, light-coloured bands ranging from a few millimetres to more than 100 mm in thickness; the thinnest of these bands probably represent transported volcanic ash from minor eruptions anywhere within the catchment, whereas the thicker bands commonly show lapilli structure (Figure 6.3), indicating airfall deposition directly into the lake. Features associated with the tuffs in the mudstone are pyritic concretion layers, suggesting temporary sulphate-enrichment of lake waters, thin horizons of disrupted bedding which may be of seismic-induced origin, and thin horizons of coalified leaves and twigs which may represent tephra-damaged vegetation. Several tuff bands were found to be cemented by the rare

Table 6.1 Major element analyses for Paparoa Coal Measures mudstones, Greenland Group, and "Morgan volcanics", all expressed on a loss on ignition free basis.

Sample	MgO	Na2O	SiO2	Al2O3	SO3	P2O5	Fe2O3	MnO	TiO2	CaO	K2O		
WM1	1.91	0.00	64.90	21.57	0.51	0.09	5.68	0.05	1.02	0.08	4.14	31	55
WM2	3.05	0.00	58.17	21.49	0.00	0.06	11.60	0.05	0.99	0.09	3.36	37	80
WM3	2.15	0.00	61.21	23.34	0.18	0.06	8.14	0.09	0.97	0.10	4.63	53	67
GM1	1.74	0.00	64.82	20.74	0.00	0.30	5.88	0.07	1.05	0.24	3.69	285	74
GM2	1.78	0.00	71.17	17.19	0.00	0.21	5.17	0.07	0.98	0.22	3.20	193	69
PRM1	1.43	0.00	67.82	22.70	0.00	0.00	2.67	0.03	1.08	0.10	4.63	60	85
Zgl G	2.42	1.50	76.86	13.40	0.00	0.14	4.78	0.00	0.67	0.54	3.14		
Zgl A	3.19	1.60	71.55	13.87	0.00	0.22	6.36	0.00	0.30	0.97	2.97		
WMt1	2.64	0.00	53.59	20.60	0.50	0.90	13.68	0.12	3.16	1.68	2.18		
WT1	0.41	0.26	40.75	27.67	0.11	10.30	1.76	0.02	3.28	14.79	0.63		
WT2	9.15	1.50	43.71	12.78	0.00	0.55	12.54	0.32	3.09	12.77	2.02		
B1	8.45	2.79	44.73	12.41	0.00	0.90	12.37	0.17	3.81	10.26	1.48		

Samples:

WM1-PRM1 : Waiomo, Goldlight, Rewanui and Pike River mudstones described in Table 6.1 .

Zgl G Greenland Group from north of Greymouth Coalfield. Average of greywacke sample P39127B and P39799 from Nathan (1976)

Zgl A Greenland Group, as above. Average of argillite samples P39131A and P39798 (Nathan).

Wmt 1 Coarse tuffaceous aggregate from Waiomo Member, Greymouth Drillhole 631.

WT 1 Wilkeite-bearing lapilli tuff from Waiomo Member, Docherty Creek, Greymouth.

WT 2 Tuffaceous Waiomo Mudstone, Drillhole 632, 647metres, Greymouth.

B1 Basalt from flow underlying Paparoa Coal Measures, Pike River Coalfield.

Table 6.2 Sample and mineral data for mudstones from Paparoa Coal Measures, Greymouth and Pike River Coalfields. Q quartz I illite K kaolinite Chl chlorite S siderite

	SAMPLE DESCRIPTION	SAMPLE TYPE	MINERAL ASSEMBLAGE (XRD)	PRINCIPAL SILICATES, NORMALISED TO 100% (XRD) Quartz	Kaolinite	Illite	(CALCULATED) Quartz	Kaolinite	Illite
WM1	Waiomo Mudstone Member DH 621, 362m	S	Q..I>K>Chl>S	44	12	44	39	12	49
WM2	" " " DH 624, *1	S	Q>I>K>Chl>>S	47	17	36	36	20	44
WM3	" " " DH 632, 598m	S	I>Q>K>Chl>S	39	12	49	33	11	56
GM1	Goldlight Mudstone Member DH 614, 104m *2	S	Q>I>K>Chl>S	46	15	39	41	14	45
GM2	" " " DH 614, 140m	S	Q>I>K>Chl>S	54	16	30	52	10	38
GM3	" " " DH 660, 40.3m	S	I>Q..K>S>Chl		n.d.		27	25	48
GM4	" " " DH 660, 71.5m	S	I>Q..K>S>Chl		n.d.		36	19	45
RM1	Mudstone, Rewanui Member DH 660, 179.5m	S	I>Q>K>>Chl..?Feldspar		n.d.		42	14	44
PRM1	Pike River, Member 5 mudstone	S	I>Q>K>Chl	35	14	51	38	9	53

*1 May include some material of tuffaceous origin *2 Sample J31/s7B of Nathan & Smale (1983).

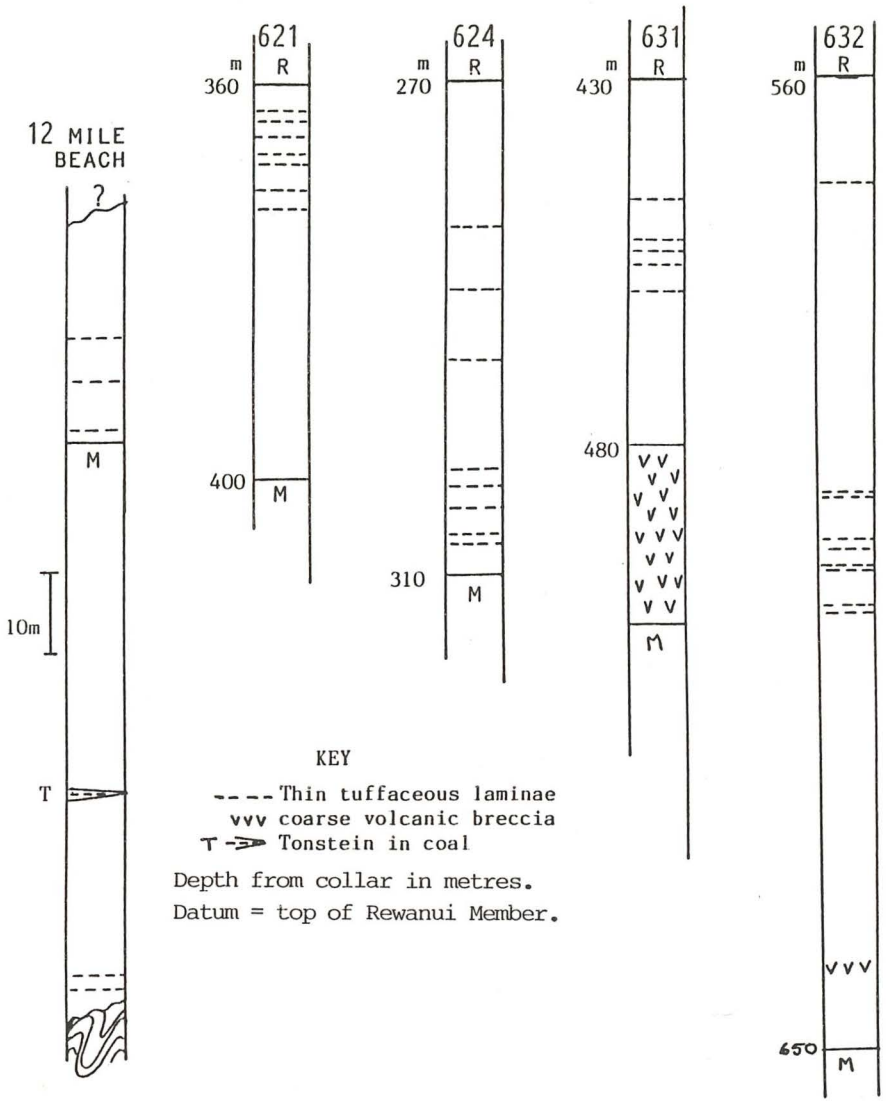
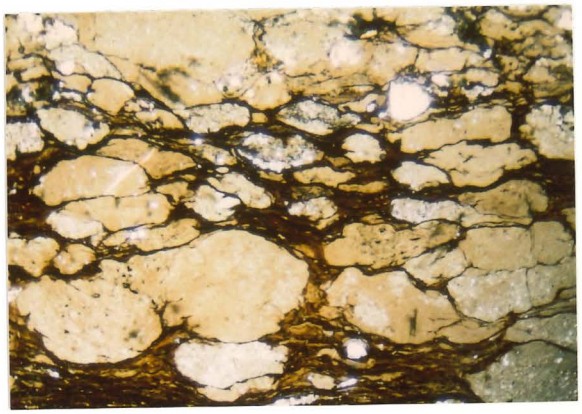


Figure 6.2 Distribution of volcanic horizons in western-central localitiies of Greymouth Coalfield. R = Rewanui M = Morgan

a

(b) Kaolinitised lapilli tuff in carbonaceous mudstone. Thin section, ppl, x25.



b

Figure 6.3 Tuffs in coal and lacustrine mudstone, Paparoa Coal Measures, Greymouth Coalfield.
(a) Top: Lapilli tuff in Waiomo Mudstone Member, Docherty Creek. This specimen contains wilkeite (c.f. hydroxyapatite) as a cement.
Lower right: Tuffaceous sediment in Waiomo Mudstone drillcore, showing a light-coloured band and pyritic nodules.
Lower left: Kaolinitised tonstein of volcanic origin in Morgan coal, 12 Mile Beach.

mineral wilkeite, which is classified as an intermediate between hydroxy-apatite, $3Ca_3P_2O_8.Ca(OH)_2$, and ellestadite, $3Ca_3SiSO_8.Ca(OH)_2$ (Winchell and Winchell, 1951).

Analyses of basalt, tuffaceous breccia, and tuffaceous mudstone from the Paparoa Coal Measures are included in Table 6.1, together with analyses for a number of non-tuffaceous mudstones.

The few tonsteins found in Morgan coal are considered to be of volcanic origin on the following evidence:

(i) Well developed lapilli structure, which in thin section reveals sparse euhedral zircon in a kaolinite matrix. Identical lapilli structure can be seen at Pike River Coalfield, occurring at the base of coal seams and grading downwards into massive tuffs.

(ii) Identical lapilli structures are also present in some of the tuffs occurring in lacustrine mudstone. Analysis of some of these tuffs reveals a basaltic composition (Table 6.1).

(iii) The tonsteins occur abruptly in low ash coal, where there is no evidence of detrital or chemical sedimentation.

(iv) Tonsteins are restricted to coal of the Morgan Coal Measures Member, and its probable correlative at Pike River Coalfield; these coals are the only ones known to be contemporaneous with nearby volcanic activity.

6.2.3 Granite

Granitic sediment first appears at Greymouth in the Rewanui Member, and at Pike River in Member 4. At both localities, granite remains an important sediment component during later coal measure sedimentation, although it is less conspicuous in the Dunollie Member as a result of greater weathering prior to deposition (Gage, 1952) .

No attempt has been made to identify the source of granite debris supplied to the Paparoa Coal Measures. A minor northwestern source was located beyond the present coastline, while "axial" sources, presumed to lie somewhere to the northeast of Greymouth Coalfield (Newman, 1985a), could include one or more of several plutons of the Karamea Batholith composite. Gneisses of the Charleston Metamorphic group are

probably also represented in the granitic sediment. It is considered unwise to attempt to relate the composition of these granites to the Paparoa sediments until a study of granite clasts within the coal measure rocks is carried out.

Petrographic descriptions of Greymouth coal measure sandstones have been provided by Smale (1978), who shows that the Rawanui Member is the only unit containing abundant alkali feldspar of granitic origin, and that most of the feldspar in the sandstones is substantially altered by weathering. A more persistent indicator of granitic sediment is coarse muscovite, which occurs as fresh flakes in both Rewanui and Dunollie Members.

6.2.4 Coal Measure Mudstones as an Indicator of Source Material.

Nine mudstone samples from the Paparoa Coal Measures have been analysed for major elements, which have been expressed on a loss-free basis in Table 6.1. It can be argued that the lacustrine mudstones provide the nearest equivalent to an ideal, "average" fine sediment which might be carried into swamps by floodwaters. Although a group of only 9 samples provides a limited statistical base, the analyses suggest a high degree of uniformity in mudstone composition, probably in response to considerable mixing during transport. It is particularly notable that, with the exception of phosphorus, the analyses show a strong similarity between Waiomo and Goldlight mudstones, despite the source rock differences for these two units. Samples from the Waiomo Mudstone (WM1-WM3) should represent a Greenland Group source, but could also contain some volcanogenic material. However, the other samples, taken from overlying units, could represent either Greenland Group or granite, or some mixture of these sources. Basin history studies by Newman (1985a) suggest that Goldlight Mudstone accumulation in western areas of the coalfield was dominated by Greenland Group sedimentation (samples GM1, GM2), whereas mudstone in the axial region, further east, should contain a granitic element (GM3, GM4, RM1). The Pike River mudstone (PRM1) came from a unit interbedded with granitic sandstones, and should represent granitic sediment.

One of the analysed mudstones (RM1) was taken from a silty lithology within the the upper part of the Rewanui Member, but is very similar in composition to the lacustrine mudstones, except for a higher sodium content. It should be noted that the mudstones will fail to represent coarser sediments, which may be an important source of mineral matter in some coals.

Additional major element analyses for fine grained rocks of the Paparoa Coal Measures have been reported by Nathan and Smale (1983). One of these samples (GM1, Table 6.1) was re-analysed by the writer who found a poor comparison with the earlier values. Because it is known that the analyses quoted by Nathan and Smale were obtained from XRF of whole rock powder, and that no matrix corrections were applied, these older results have not been used.

6.3 DEPOSITIONAL ENVIRONMENT

Depositional environments for the Paparoa Coal Measures are described in detail by J. Newman (1985a, 1987), although this work is largely restricted to the Rewanui Member at Greymouth. A wide range of depositional settings are represented by the Coal Measures as a whole, and it is not appropriate to present more than a brief summary of Newman's findings here.

Two major peat-accumulating environments favourable to coal seam development are distinguished, i.e.,

(i) low-lying areas near lake margins, and

(ii) areas on a fluvial flood plain which were sufficiently low-lying to permit swamp development, yet sufficiently isolated from active channel zones to avoid frequent incursion by sediment.

Various combinations of these settings are described, e.g., development of locally ponded areas on the floodplain, and formation of deltaic zones at lake margins. On the basis of coal petrology, vitrinite reflectance, and volatile matter yield, Newman distinguished 4 coal "type classes", considered to result from different swamp environments, as follows:

Type I: Evidence of an autochthonous peat containing resinous and waxy macerals attributed to a "conifer" element; general indications are of a high, but non-stagnant water table.
Type II: Evidence of predominantly autochthonous peat, containing undisturbed inertinite horizons and some reworked and oxidised peat clasts interpreted to result from periodic dessication; other evidence of relatively low water table and good drainage.
Type III: A detrital, transported assemblage of macerals with or without mineral matter. Fragmented inertinite is common and a hypauthochtonous origin is inferred. A generally low mineral matter content (in the samples examined) is attributed to isolation from major channels, but sparse, coarse grained quartz is present and is regarded as originating from floating vegetation. A consistently high water table and stagnant drainage conditions are inferred.
Type IV: An unusual type comprising an entirely allochthonous accumulation of fragmented macerals including abundant inertodetrinite. A lake margin setting is postulated.

Except for the unusual type IV, the hypautochthonous type III can be expected to have the greatest potential to include coarse sediment washed in from external sources, and to contain quartz-rich mineral matter. However, the relationship may not exist where sediment-bearing streams had no access to the swamp, as suggested by Newman. Type II, being the most "emergent" and well drained class, can be expected to have been accompanied by strongly leaching conditions. "Good drainage", as used in this thesis, can be defined as unrestricted passage of meteoric or other water through the peat, and does not imply persistent aeration of the peat surface, which would produce abundant inertinite. Well drained conditions are particularly important to discussion of some Brunner coals, and are discussed more fully in that context (7.6).

6.4 INTERPRETATION OF ANALYSES

6.4.1 Comparison of Mineral Matter and Coal Measure Sediments

A qualitative, but direct comparison of mineral assemblages in coal and coal measure sediments can be readily made. Tables 4.2, 6.2, and Figure 6.4 demonstrate the following differences between lacustrine mudstone and typical mineral matter in coal:

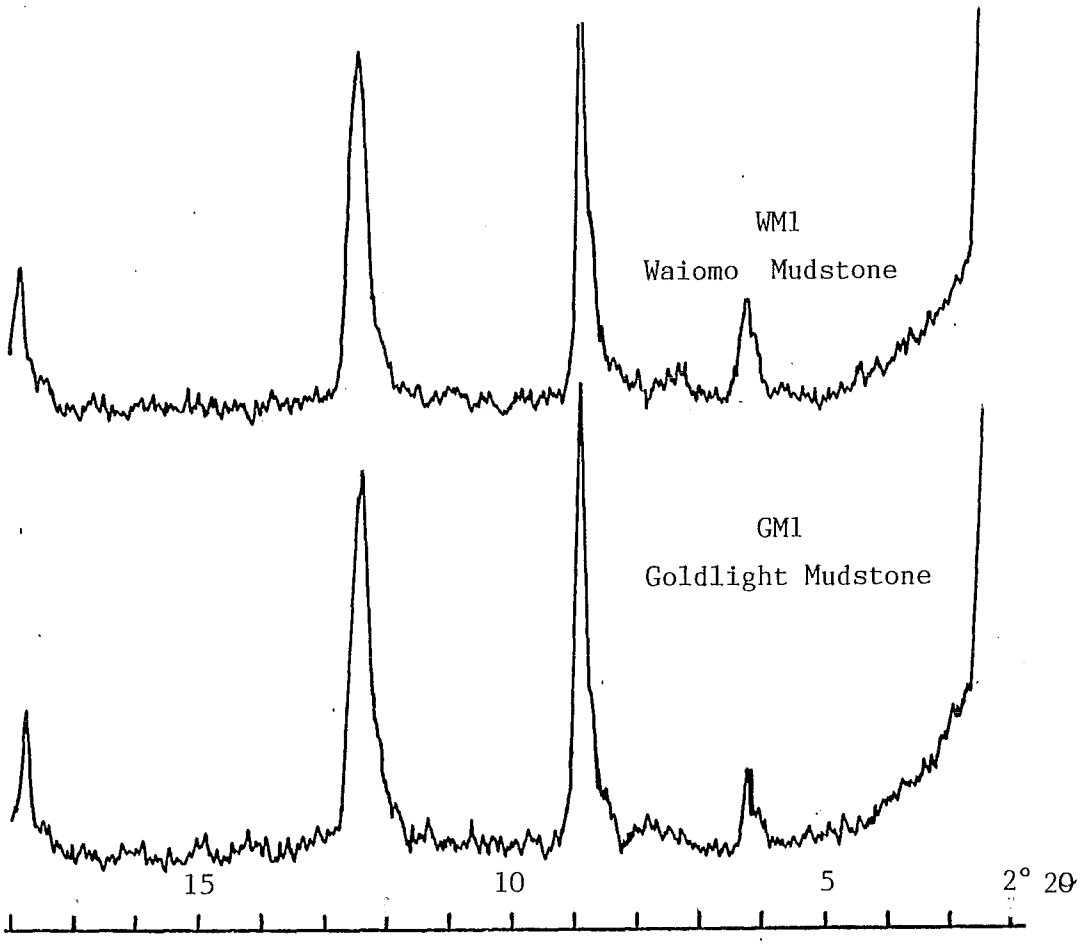


Figure 6.4 XRD traces for lacustrine mudstones from the Paparoa Coal Measures (air-dried smear mount).

(i) The mudstones generally contain more illite, which is dominantly micaceous ("sericitic").
(ii) The mudstones all contain minor chlorite, which is rare in Paparoa coals.
(iii) The mudstones contain less kaolinite, which is of lower crystallinity than kaolinite in coal.

Coarser coal measure sediments have a mineralogy similar to the mudstones, but contain more quartz and coarse muscovite, and occasionally some K-feldspar (Rewanui and overlying members). Feldspar is unknown in the coals, but flakes of muscovite have been noted in LTA residues.

The tonsteins in coal consist almost entirely of well crystallised kaolinite. By comparison, the tuffs from the mudstones contain, in addition to a major kaolinite component, siderite, calcite, dolomite, quartz, illite, and in some cases, wilkeite.

Chemical analysis provides a quantitative basis for comparing coal mineral matter and fine grained sediment. Figure 6.5 shows the abundance distribution of most ash constituents in Greymouth drillhole samples. Also shown are points for averaged values from both Liverpool and Strongman run-of-mine coal, and for averaged mudstone composition.

The spread shown by these distributions is exaggerated by a dilution effect caused by widely varying abundances of quartz and siderite. Quartz variability is demonstrated by the distribution of SiO_2, which is broad and diffuse, in comparison to that of Al_2O_3 which is comparatively narrow and sharp.

Fe_2O_3 in ash varies widely in response to the erratic distribution of siderite in coal. TiO_2 in ash also varies about the mudstone average, and shows that the Liverpool Mine (Morgan Member) values greatly exceed those of Strongman Mine (Rewanui Member).

Both P_2O_5 and Na_2O are generally higher in ash than in mudstone,

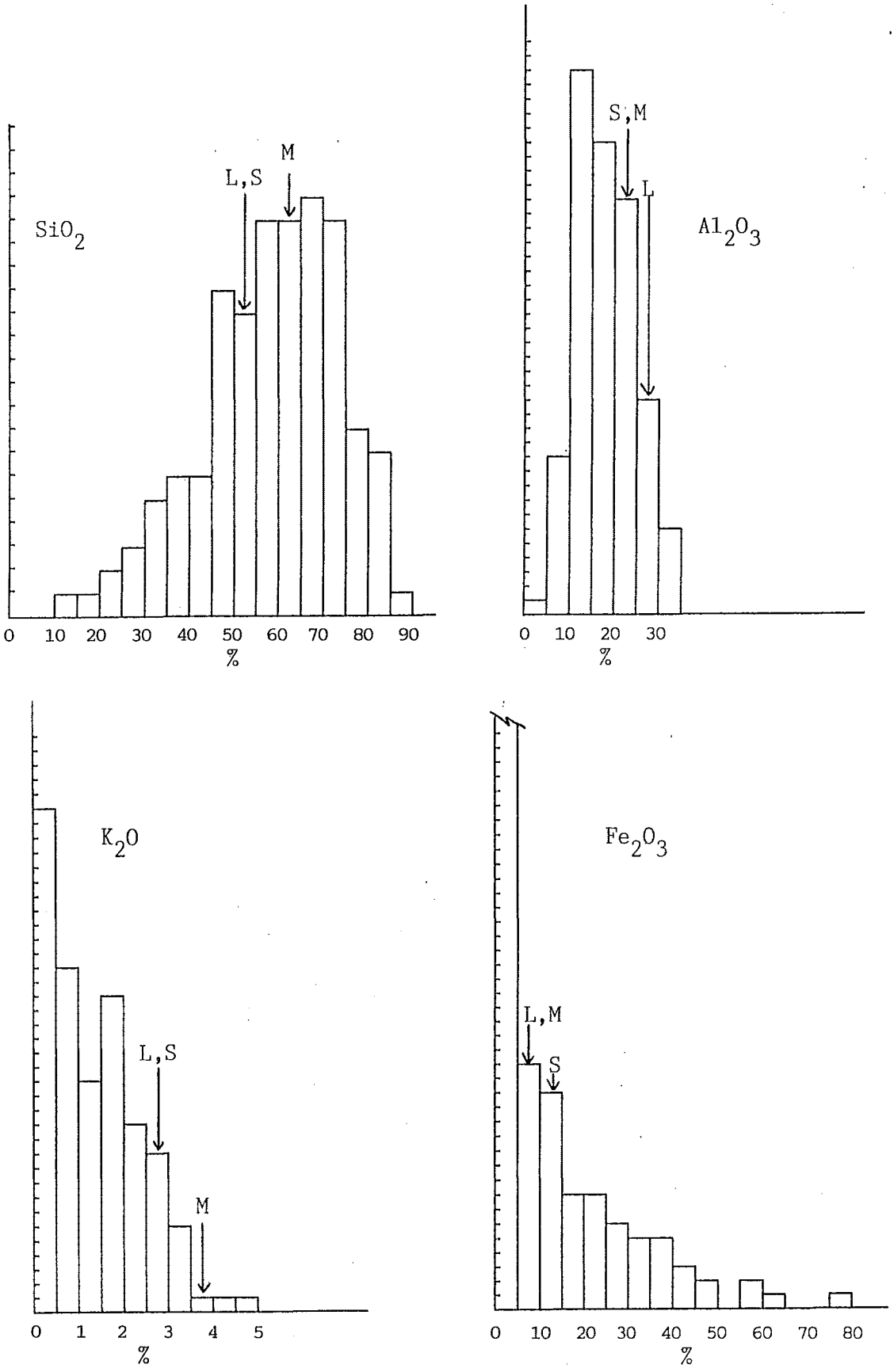
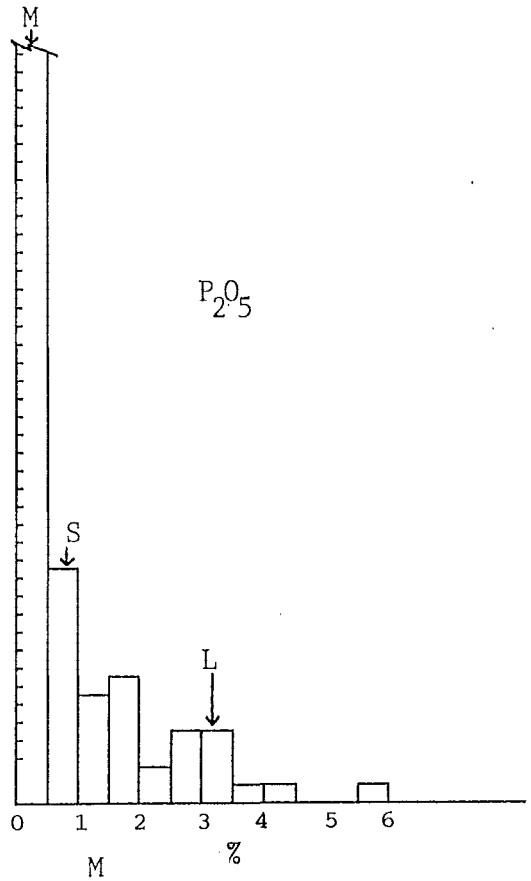
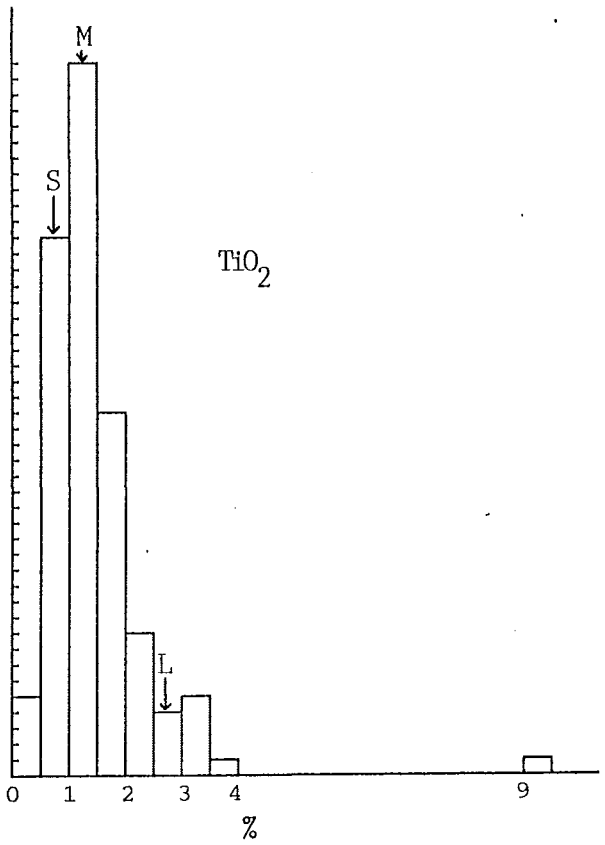


Figure 6.5 Abundance distributions for ash constituents, Rapahoe Sector Rewanui coals. M = average of 9 coal measure mudstones;
L = average, Liverpool Mine (Morgan Member);
S = average, Strongman Mine.
Each vertical division = 1 sample





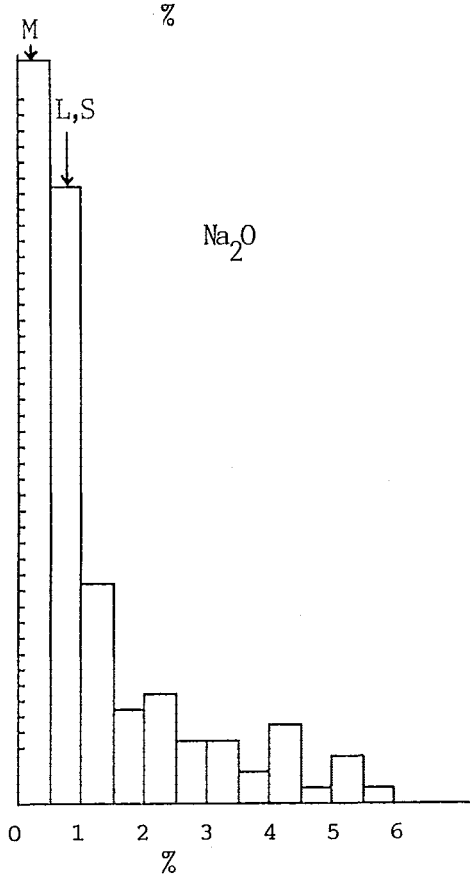


Figure 6.5 continued.

although peak distribution for ash in each case lies within the lowest interval. The possible factors controlling P_2O_5 concentration in ash are discussed in detail later in this chapter. Na_2O has a strongly organic association, and the distribution profile for this component in Figure 6.5 is largely a result of variation in total ash yield.

A further comparison between mineral matter and sediment is possible by considering the trends shown by the sink-float fractions of Pike River sample 27/531. Unlike the other sink-float Paparoa samples, this coal contains no coarse authigenic minerals, and exhibits regular, well defined geochemical trends in the density fractions (Figure 5.1). Where the trend at high ash is clearly defined, the intercept at a point equivalent to 100% ash predicts the composition of mineral matter which can be physically separated from the coal by gravity methods.

Table 6.3 compares the predicted composition of "separable minerals" with the mudstone analyses. The similarity between "minerals" and mudstone with respect to SiO_2, Al_2O_3, and K_2O, suggests that the raw sample contains a significant proportion of relatively unaltered mudstone. The relative decline in K_2O content of ash from the float fractions parallels a progressive change in illite composition. Illite in all mineralogically analysed fractions of sample 27/531 shows a relatively large interlayer component, which may contribute to the higher Na_2O value in the "mineral" composition. The extremely low Na_2O values for most coal measure mudstone samples contrasts with the higher values in Greenland Group rocks (ca. 1.5%, Table 6.1), and the values expected from granite - derived sediment. It must be assumed that all sodium minerals become highly unstable in the coal measure environment.

CaO is distinctly enriched in the coal "minerals", whereas MgO is not. These components almost certainly entered the peat as silicates (micas, chlorites), and dissolved in groundwater, and now appear in the sinks as authigenic carbonates. A highly variable distribution of these minerals obscures depletion/enrichment trends for CaO, MgO, MnO and Fe_2O_3.

Table 6.3 Predicted composition of mineral matter separable from Pike River sample 27/531, compared with the composition of coal measure mudstones.

	27/531 "Minerals"	Mudstone Average	Pike River Mudstone
MgO %	1.6	1.9	1.4
Na_2O %	0.75	<0.05	0
SiO_2 %	65	64.1	67.8
Al_2O_3%	21	21.9	22.7
P_2O_5 %	<0.01	0.14	0
Fe_2O_3%	2.6	6.3	2.7
TiO_2 %	0.3	1.1	1.1
CaO %	1.8	0.1	0.1
K_2O %	3.4	3.9	4.6
Sr ppm	?<200	110*	60
Ni ppm	~40	72*	85

Both TiO_2 and nickel are depleted in the "mineral" fraction with respect to mudstone composition, indicating that these components tend to become leached from sediments and associated with organic matter. However, the trend for P_2O_5 is not clear. The very low value for the coal "minerals" is significantly less than the mudstone average, but the Pike River mudstone contained undetectable (< 0.05%) P_2O_5. If this mudstone analysis is regarded as anomalously low, the coal minerals can be considered P_2O_5 - depleted.

6.4.2 Al_2O_3 / SiO_2 Ratios

A graph showing all Greymouth Paparoa coal samples plotted against Al_2O_3/SiO_2 axes (Figure 6.6) shows a very large degree of scatter, as previously described in section 5.3. Additional data shown in Figure 6.6 include points for Liverpool and Strongman run-of-mine samples, a channel from the Tiller Mine (Dunollie Member), and the coal measure mudstones.

In terms of Al_2O_3/SiO_2 ratio, points are scattered both above and below the mudstone field, but few fall near the kaolinite limit. Because simple kaolinite - illite mixtures would plot between the radial lines, dispersion of points away from this zone must be interpreted as indicating an increasing quartz component. If the mudstone composition can be considered to represent fine sediment entering the swamps during flood-

ing, all points which exhibit Al_2O_3/SiO_2 ratios significantly higher than the mudstones can be expected to represent the effects of either deposition of authigenic kaolinite, or loss of silica by leaching. Such leaching could occur directly within the swamp or in a soil horizon which supplied sediment to the swamp. Similarly, samples which plot below the mudstone field can be considered to have either gained authigenic silica, or received quartz-rich sediment, probably silt or sand.

Density fractions of a Strongman Mine sample show that silica tends to increase in the low-ash coal, suggesting the presence of fine-grained authigenic quartz (sample 37/016, Figure 5.2). Although this may contribute to the silica-rich character of the samples which plot below the mudstones in Figure 6.6, petrographic evidence suggests that detrital quartz is more significant in this respect.

Some of the scatter on the Al_2O_3/SiO_2 plot might be attributed to differences between drillcore samples and the more homogeneous, selectively mined Liverpool and Strongman products. However, nearly all the drillcore composites were washed, where necessary, to provide coal at or less than 7% ash, prior to analysis. A plot of SiO_2 in whole coal against ash (Figure 6.7) confirms that the trend for Rapahoe Sector drillcore samples is distinctly siliceous in comparison to the Strongman and Liverpool coals. Furthermore, the silica-rich limit of the field increases with ash, suggesting that any significant authigenic silica content was derived by redistribution of silica within the coals; introduction of authigenic silica from external sources would be expected to affect the inorganic composition of low ash coals to a greater extent than for high ash samples.

Whereas the Tiller Mine sample (Dunollie Member) shows an extremely low silica trend in Figure 6.7, the Strongman and Liverpool samples appear to share a common trend, despite their location in different coal measure members. This apparent similarity may be coincidental, for on the Al_2O_3/SiO_2 plot (Figure 6.6) these samples occupy separate fields. The Liverpool samples can be seen to be more tightly clustered, and more Al_2O_3-rich than the Strongman group. On the same plot, the Tiller Mine sample falls very near the kaolinite limit.

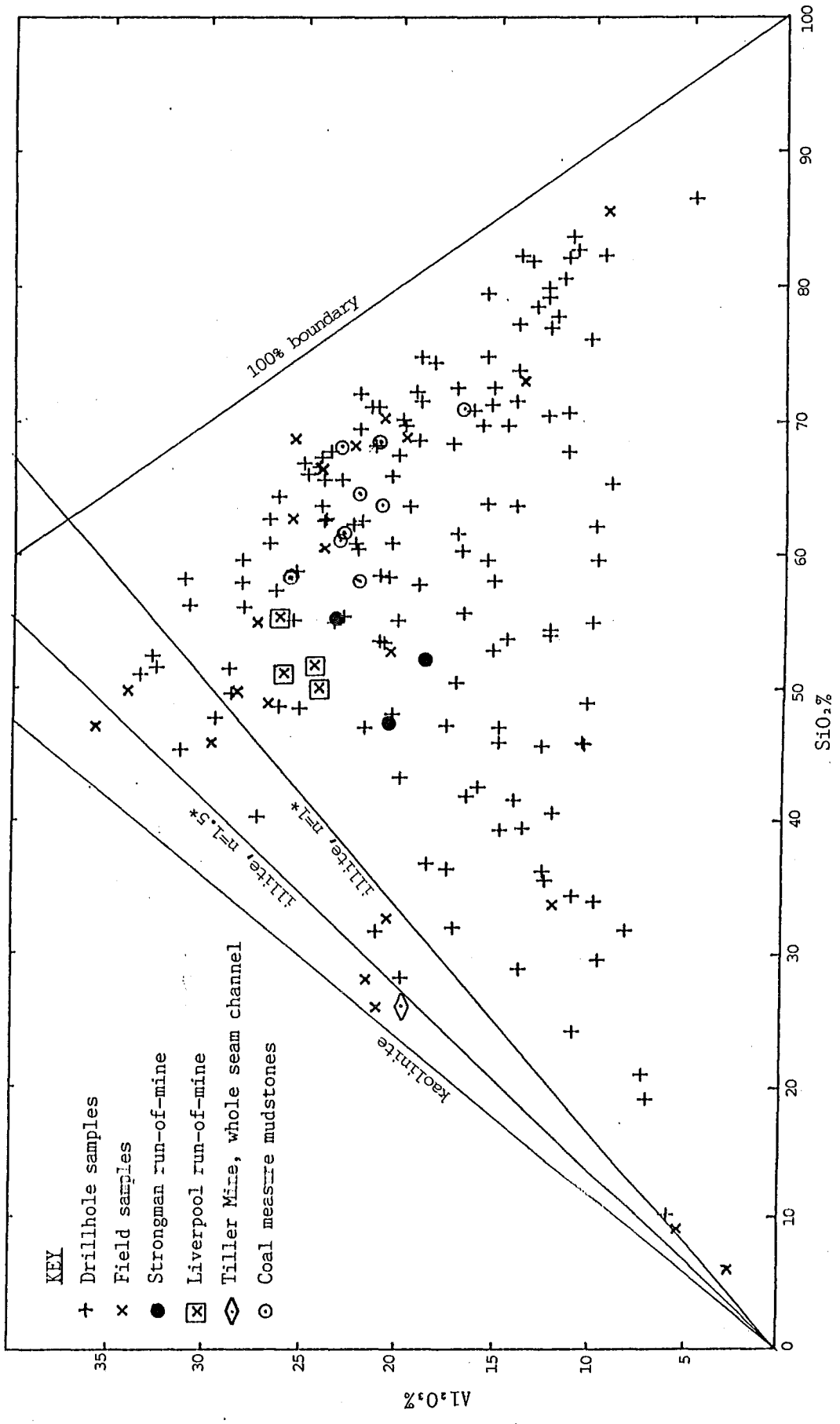


Figure 6.6 Composite graph of Al_2O_3/SiO_2 for all Paparoa samples from Greymouth Coalfield. *see discussion of illite composition in Section 2.6.2.

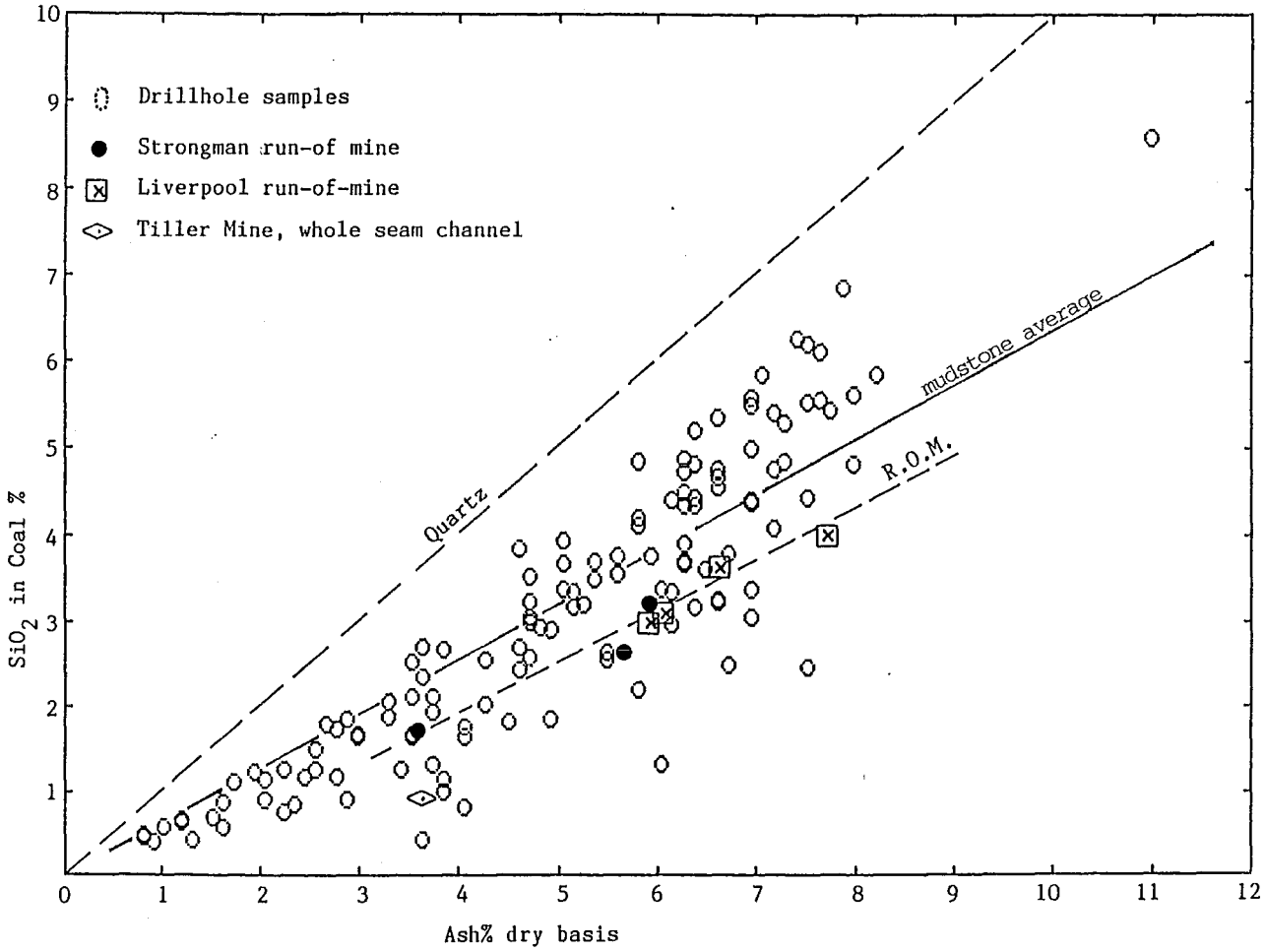


Figure 6.7 SiO_2 in whole coal vs ash for all Rapahoe Sector drillhole samples and run-of-mine samples. Tiller Mine sample represents a full-seam channel.

6.4.3 Quartz-Kaolinite-Illite Variation

To remove the dilution effect of authigenic carbonate minerals, calculated mineral assemblages for the coals have been plotted on quartz-kaolinite-illite variation diagrams.

Greymouth run of mine samples and field samples are plotted in Figure 6.8, together with a field defined by the coal measure mudstones. Points for spot and ply samples are scattered widely, but provide some useful contrasts. Three Rewanui roof coal samples of medium to high illite content show a variation in calculated kaolinite from nil to more than 50%. The sample for which kaolinite is calculated as nil can be shown by XRD to contain a small amount of modal kaolinite (P19, Tables 4.2, 4.4), and the discrepancy between actual and calculated kaolinite can be attributed to the presence of an unusual abundance of fresh

muscovite, sufficiently K_2O-rich to cause over-estimation of calculated illite. This material was deposited during the final phases of the peat swamp, and probably represents micaceous silt supplied by increased current energy when the peat was overwhelmed by sediment. Furthermore, rapid burial by succeeding beds would prevent significant weathering of this material.

The mudstones, Strongman coals, Liverpool coals, and the Tiller Mine sample all plot in the same relative positions in Figure 6.8, as they occupy in Figure 6.6, but the fields are more clearly defined. The mine samples define a progression from the mudstone field towards the kaolinite apex, with little change in the quartz-illite ratio. The spread of plotted fields is presumably the net result of a number of environmental factors, which govern the character of sediment entering the swamps, the extent of alteration in the peat, and the degree to which authigenic kaolinite formed from solution.

All Rapahoe Sector drillhole samples, including the ply samples from Drillholes 628 and 633, are represented in Figure 6.9. The wide spread of values which characterises this group is present. Most of the points occupying the kaolinite apex are plies for DH 628, and can be considered atypical of the Rapahoe Sector coals as a whole, which otherwise define a field extending as a broad zone from the mudstone field (shown on Figure 6.8) towards the quartz-kaolinite boundary, with a distinct bias towards quartz.

These trends require careful interpretation. On first consideration, the extreme variability and dominantly quartz-rich trend of the Rapahoe Sector samples might be seen as a natural consequence of the strongly fluvial character of the Rewanui Member, and attributed to hydraulically transported sediment. However, few of the Rapahoe Sector samples included in the study can be regarded as seriously contaminated by fluvial sediment, as indicated by the generally low ash values (Figure 6.6) and petrographic descriptions of Newman (1985a); washing to <7% ash was required for only a small proportion of the samples. Mineral composition of the roof coal samples suggests that contamination by silt should lead to a high proportion of illite in the mineral matter.

The best explanation for this apparently conflicting evidence is to

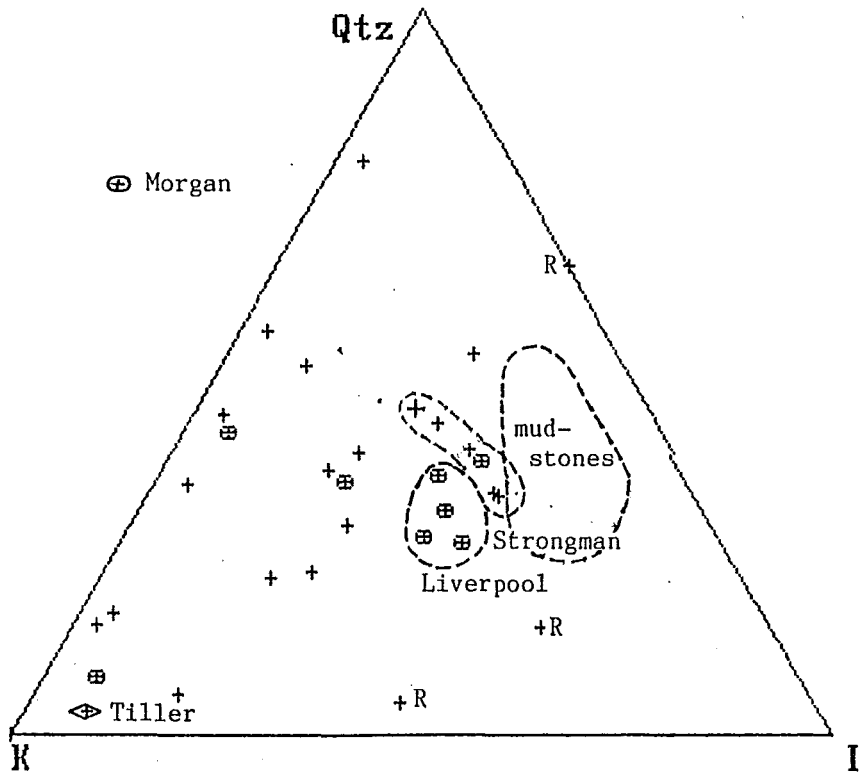


Figure 6.8 Quartz-kaolinite-illite variation diagram for Greymouth field samples and mine samples. R = roof coal samples.

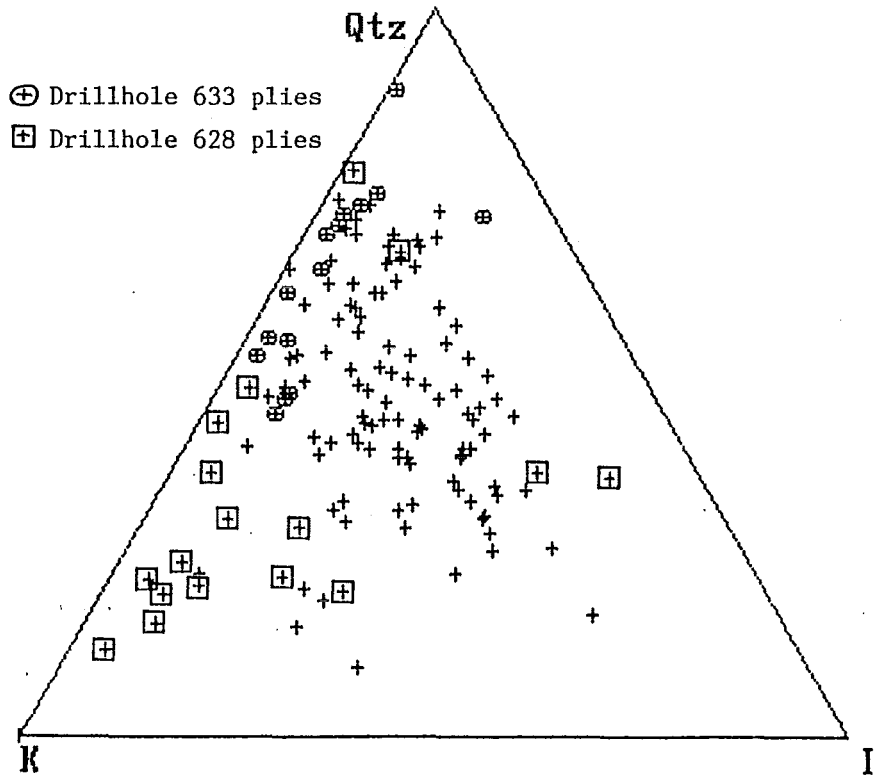


Figure 6.9 Quartz-kaolinite-illite variation diagram for all Rapahoe Sector drillcore samples.

attribute the "excess" quartz to grains dropped from, or incorporated on, vegetation which entered the swamp by rafting. There is abundant evidence of "chuckie stones" in Rewanui coals, as shown by exposed seams and by drillcore logs. Discrete and randomly distributed quartz grains seen in otherwise sediment-free Rapahoe coal in petrographic section (Newman, 1985a) probably have the same origin.

In contrast, the Dunollie coal contains no "chuckie stones", and probably negligible rafted grains. The strongly kaolinitic character of this coal reflects the low energy deposition and highly weathered sediment envisaged for the Dunollie Member depositional environment (Gage, 1952; Smale, 1978; Newman, 1985a).

Figure 6.10 shows the quartz-kaolinite-illite variation trends of the density fractions from the 3 sink-float Paparoa samples. The siliceous trend of the Strongman Mine sample is well shown, and runs against the trend of the other two samples (Tiller Mine and Pike River Coalfield southern Member 4), which plot as parallel loci, generally toward the illite side of the kaolinite apex. Floats for the Tiller Mine sample plot outside the diagram boundary as a result of a small computed boehmite content. The seams represented by these two samples are characterised by an absence of "chuckie stones", and by a high content of nondetrital inertinite in comparison to Greymouth Rewanui coals (Newman, 1985a; J Newman, pers. comm.). This evidence suggests that kaolinite formation, accompanied by loss of quartz, illite, and other silicates, is promoted by the lower water table conditions which are identified as the primary cause of inertinite development (Teichmüller, 1982).

Quartz-kaolinite-illite variation for all Pike River Paparoa samples is shown in Figure 6.11. Although the plotted data are few in number, distinctive fields for coals from Members 3 and 4 can be inferred. The Member 3 points define a broad band along the kaolinite-quartz border, consistent with incorporation of highly kaolinite-rich, illite-poor weathering products from the surrounding volcanic deposits during peat accumulation. The more quartz-rich samples are from seams known to contain sandstone partings, probably derived from local Greenland Group source areas accessed by the larger streams. Field evidence shows the volcanic cover to have been relatively thin, and exposed greywacke

basement almost certainly contributed sediment to the peat swamps.

Points representing Pike River Member 4 coals are few, but generally fall within the field defined by Rapahoe Sector samples from Greymouth. Abundant "chuckie stones" in northern Member 4 Pike River Paparoa seams, indicate that rafted grains probably influence the mineral assemblages and contribute to the scatter of plotted points.

In contrast, the 3 samples from southern Member 4 coals (triangles, Figure 6.11) plot near the quartz-poor limit of the field. These samples represent Member 4 seams in the extreme south of the coalfield where boehmite in the light fractions of 27/531, and in spot sample P33 collected nearby, suggest that some intense leaching has taken place, although whole-seam analyses show this effect to be limited to discrete horizons within the seams. All properties of Member 3 coals are extremely uniform throughout Pike River Coalfield, indicating that there is minimal lateral rank variation. On the basis of relatively low volatile matter, high vitrinite reflectance, occasional inertinite horizons, and absence of "chuckie stones", compared with northern Member 4 coals, Newman (1985a) deduces that southern Member 4 peat accumulated in relatively low water-table swamps, which experienced periodic dehydration. However, moderate ash values and a high illite content for these seams suggest occasional low-energy flooding by muddy water.

6.4.4 Distribution and Origin of Phosphorus and Titanium Minerals

P_2O_5 and TiO_2 in Paparoa coal ash span a wide range of concentration, as indicated by the abundance distributions (Figure 6.5). Some extreme concentrations in spot and narrow ply samples, which are not included in the plotted abundance graphs, reveal a very non-uniform distribution of these components throughout the seams (Tables A2.1, A2.3, Appendix 2; see also Table 4.4). P_2O_5 concentration is particularly erratic, as demonstrated by the variation among different annual samples from Liverpool Mine (Table 6.4). Surprisingly, the highest P_2O_5 and TiO_2 values recorded in Paparoa ash (6.21% and 8.34%, respectively) are from a whole-seam sample, P13. There is a poorly-defined positive cor-

Table 6.4 Summary Table of ash constituents analyses for run-of-mine coal from Liverpool and Strongman Mines. Liverpool = Morgan Member Strongman = Rewanui Member

Location	Sample	Ash	MgO	Na2O	SiO2	Al2O3	SO3	P2O5	Fe2O3	MnO	TiO2	CaO	K2O
Liverpool	21/922	7.7	1.10	0.57	51.80	24.20	0.84	0.44	7.50	0.02	2.30	2.70	2.60
"	27/156	6.1	0.97	0.41	50.21	23.87	1.47	4.33	4.34	0.00	2.92	7.75	2.23
"	27/496	5.9	1.38	0.64	51.32	25.76	0.49	1.93	9.36	0.06	2.42	3.46	2.96
"	30/337	6.7	0.87	0.44	55.20	27.18	0.18	3.56	3.32	0.00	2.61	2.81	2.78
Strongman	21/913	5.1	2.20	0.58	52.40	18.50	2.20	0.44	12.20	0.07	0.92	4.50	2.40
"	27/487	3.6	3.85	0.63	47.76	20.37	5.15	1.28	9.10	0.04	0.85	7.53	2.73
"	30/329	5.9	2.11	0.37	55.50	23.04	1.64	1.11	9.36	0.07	1.00	2.69	3.09
"	37/016	2.9	2.85	0.51	51.25	16.22	2.76	0.45	18.32	0.15	0.96	2.90	1.69

relation between P_2O_5 and TiO_2, especially among the higher values for these components, although this relationship is not always observed.

Considering P_2O_5 separately, it is not possible to recognise any satisfactory correlation of this constituent with any other, except TiO_2 as mentioned above, and Sr, as discussed in Chapter 5. At least 3 of the phosphatic "P" series field samples represent seam roofs, but ply analyses from two drillholes (section 6.5) show that this association is not consistent.

Most Paparoa coal ash is enriched in P_2O_5 relative to the mudstones. Phosphorus concentration in coal, where it occurs predominantly or entirely as crandallite, cannot be attributed directly to original detrital apatite, nor to leaching of sediment within the swamp. Similarly, underclays are poorly developed beneath Paparoa seams, suggesting that floor sediments are unlikely to have acted as a significant source of phosphorus supplied to the peat.

Laboratory studies have shown that phosphate will readily react with hydroxy-Al or Al^{3+} to form various aluminophosphate compounds of low solubility (Hsu, 1968). Crandallite forms in acid weathering environments where phosphate species can react with dissolved aluminium, and is common in kaolinite-forming environments which also contain phosphatic minerals (Altschuler, 1973). Crandallite commonly occurs in weathered phosphate deposits, but also occurs as the end product of phosphate "fixation" in kaolinitic soils (Norrish, 1968), and has been reported from a tropical swamp sediment where a biochemical origin was proposed (Cowgill et al., 1963). Although crandallite has not been described from modern peat, the known circumstances of crandallite formation suggest that this mineral formed as a near-surface deposit in Paparoa peat swamps at various periods throughout their accumulation.

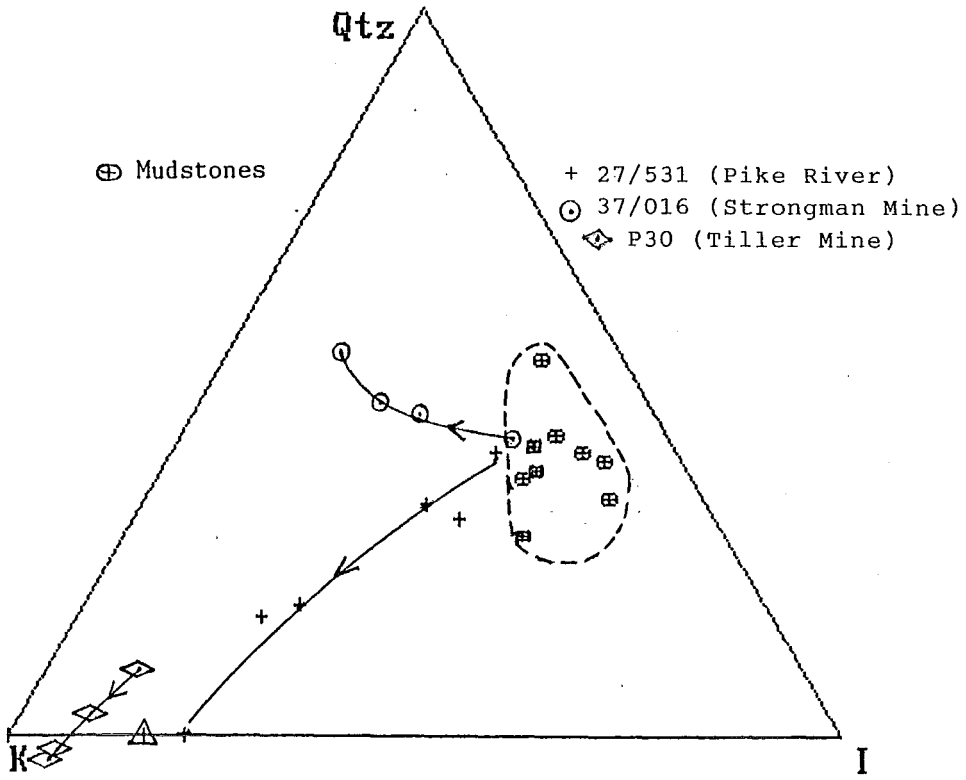


Figure 6.10 Quartz-kaolinite-illite variation diagram for sink-float fractions of Paparoa coals, in comparison with the mudstone field. The arrow shows the trend of the successively lighter fractions. Triangle = spot sample P33, from near the 27/531 sample locality.

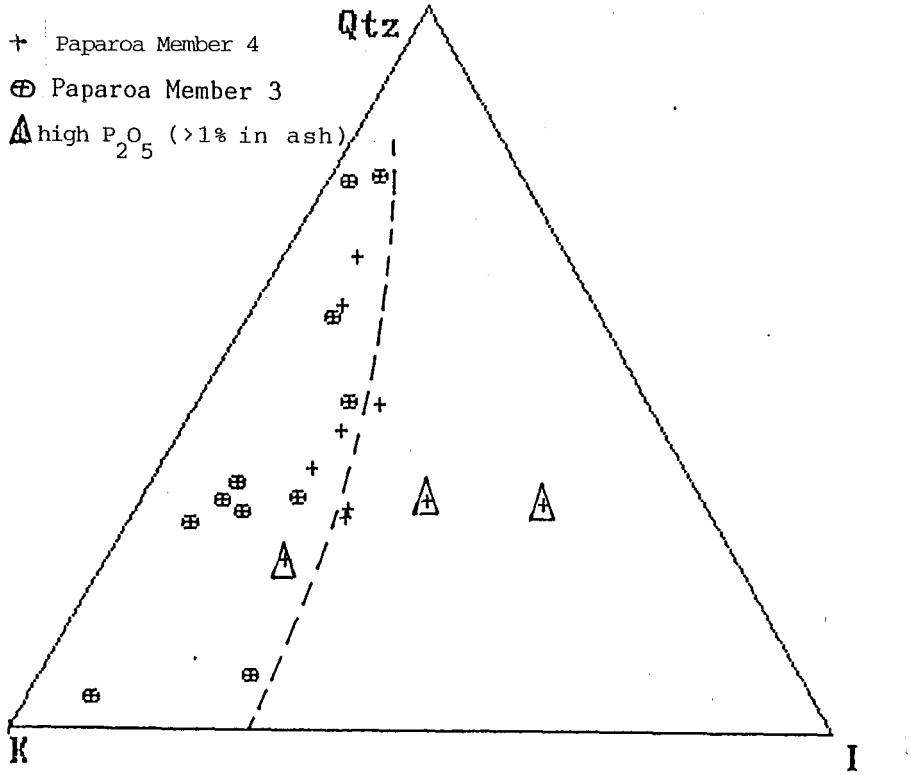


Figure 6.11 Quartz-kaolinite-illite variation diagram for Pike River Paparoa coals, Members 3 and 4.

Periodic or continuous fixation of phosphorus by crandallite formation in sediment-poor, autochthonous peat implies that phosphorus input to the swamps occurred via groundwater.

The controls on crandallite formation in peat are unknown, but probably include pH, water table level, hydroxl-Al availability, and character of the plant community. These aspects are discussed further in section 6.5, where relevant evidence from serial plies is reviewed.

Unlike phosphorus, titanium is not a major nutrient required by plant growth, and TiO_2 concentration in ash may not involve interaction with the plant community. However, it is difficult to explain TiO_2 distribution in terms of purely inorganic processes.

The analysed coal measure mudstones contain an average TiO_2 content of 1.0%, and show very little variation about this value. TiO_2 in Paparoa coal ash varies both above and below the mudstone average (Figure 6.5), but if allowance is made for dilution by high concentrations of Fe_2O_3 or SiO_2, the net trend is one of TiO_2 enrichment relative to the mudstones. TiO_2 values from run-of-mine coals (Table 6.4) show much less variability than do P_2O_5 values, but spot and ply samples demonstrate a large variation within individual seams.

Titanium enrichment by solution processes must be considered the most likely origin of extreme TiO_2 values found in Paparoa coal ash. Several studies have described examples of titanium-rich coal for which physical incorporation of mineral matter cannot be envisaged, e.g., within discrete tree trunk vitrains (Jones and Miller, 1939), and within discrete macerals on a microscopic scale (McIntyre et al., 1985). Chemical studies of peat show that the ionic titanium is readily adsorped onto humic acid exchange sites. Unlike most other metals, titanium in peat rapidly undergoes a change in bonding character to become non-exchangeable. Factors controlling adsorption are temperature, and the competing effect of other cations, chiefly K^+, Na^+, Al^{3+}, and also H^+; rising pH, therefore, favours adsorption (Eskenazy, 1972).

Local environmental control by swamp character can be expected to have exerted a major control on the incorporation of both phosphorus and titanium in Paparoa peat. However, source rock differences may also have been influential in determining the overall values which are seen in run-of-mine coal or full-seam composites. TiO_2/Al_2O_3 ratios for samples of this type show a wide separation of samples from different areas (Figure 6.12). Averaged, absolute P_2O_5 values for the mine samples vary sympathetically with Al_2O_3 ratio. In view of the relatively high P_2O_5 and TiO_2 content of the Morgan Member volcanic rocks (Table 6.1), and the relatively rapid weathering rate typical of these lithologies, it can be assumed that the volcanic source influenced mineral matter composition in Morgan peats which received erosion products from these rocks. Contribution by ashfalls may also have been significant. The similarity of mineral assemblages in Liverpool and Strongman coals (e.g., Figure 6.8) suggests that the Morgan seam at Liverpool mine received little sedimentary input from the volcanic area, which lay further to the northeast. Isopachs of the Morgan Member (Gage, 1952) show that very rapid subsidence near the margin of the coalfield has preserved the volcanics in a localised trough near their source, substantially reducing the amount of volcanic material supplied to the fluvial systems. Furthermore, at the time of peat accumulation in the uppermost Morgan Member in the Liverpool Mine area, tectonic and volcanic activity appear to have declined, and much of the volcanic material near the present Liverpool Mine may have been buried by other sediment.

Some of the abandoned mines near Roa worked Morgan seams which were closely associated with volcanic sediments. Old analyses for run-of-mine coal from the Paparoa Aerial Mine (a split upper Morgan Member seam) have been plotted on Figure 6.12, and show values for TiO_2 in ash which are extremely high, whereas P_2O_5 is slightly less than the Liverpool average.

A similar pattern can be observed for the Paparoa coals from Pike River Coalfield (Figure 6.13). High TiO_2/Al_2O_3 ratios and some high P_2O_5 values are most common for the lowermost, volcanic-influenced Member 3 seams, whereas Member 4 ashes plot nearer to the average mudstone composition.

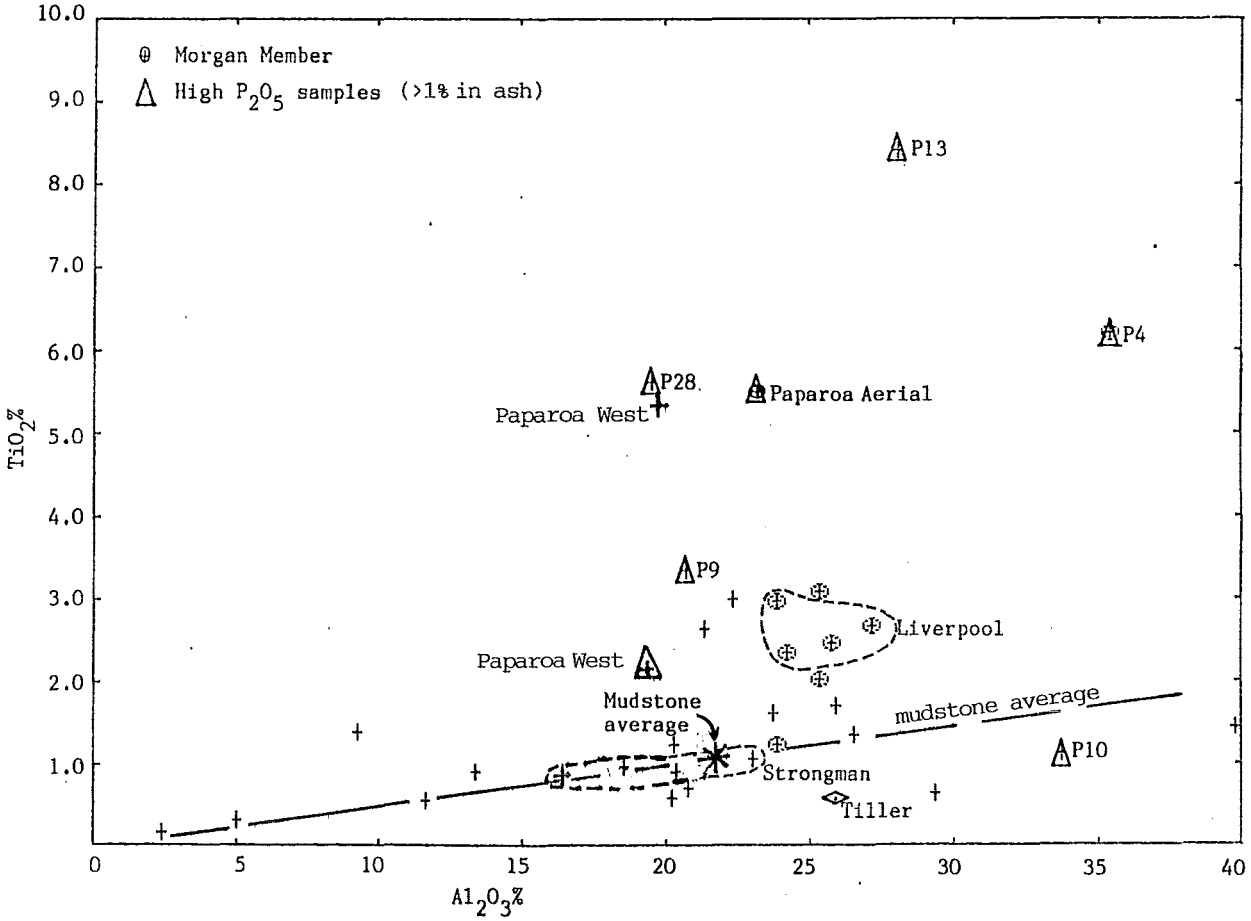


Figure 6.12 TiO_2 vs Al_2O_3 for Greymouth Paparoa 'spot samples', and run-of-mine samples. "P" samples are described in Table 4.2. Paparoa Mine analyses from Gage (1952)

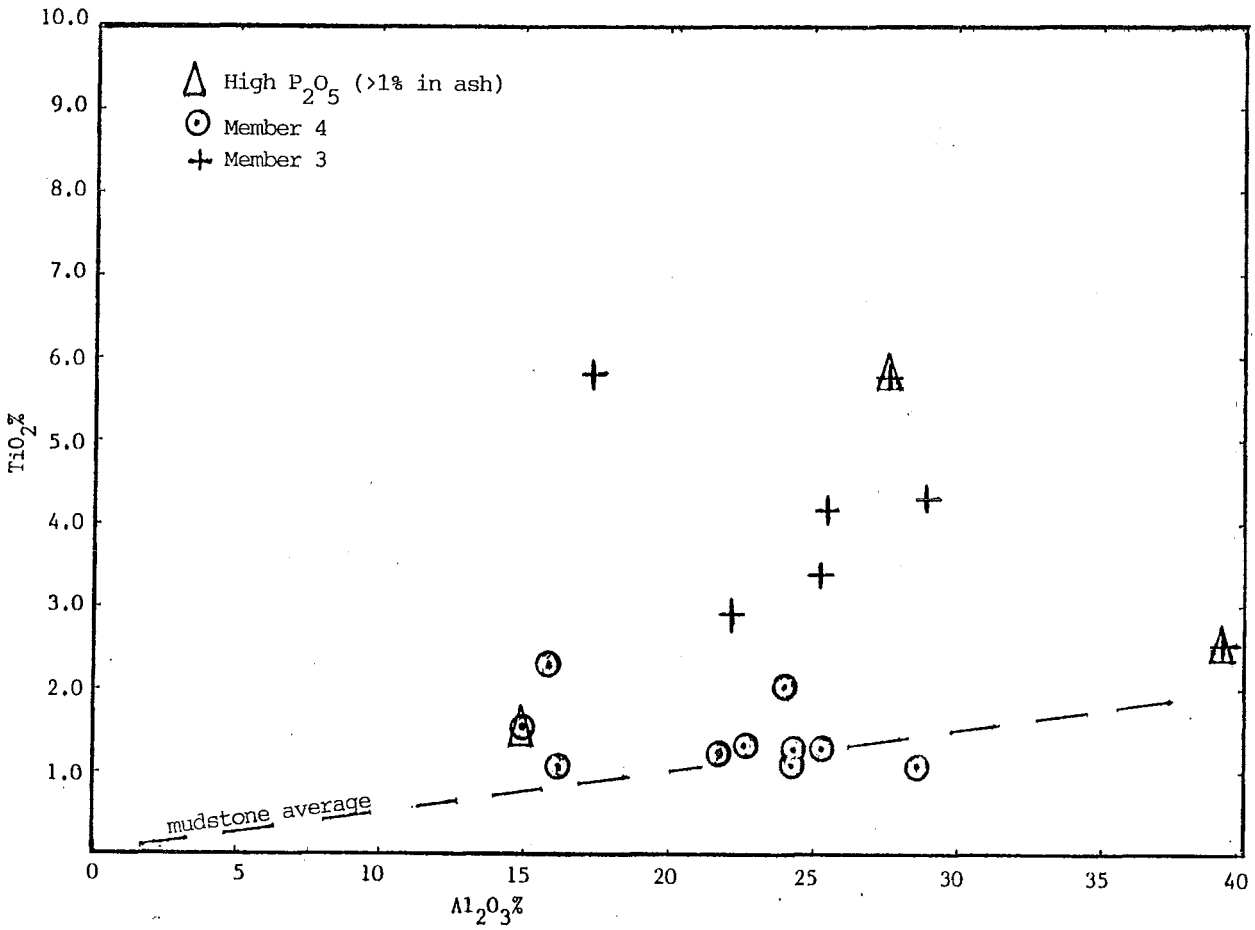


Figure 6.13 TiO_2 vs Al_2O_3 for Pike River Paparoa full seam (CRA) samples only.

It must be stressed that many of the Rewanui Member coals also have high P_2O_5 and TiO_2 values. Some of the more extreme examples (e.g. P9, P13, P24) are from the lowermost Rewanui Member in the northeast of the Greymouth Coalfield. Two ash analyses for the Paparoa West Mine, located in the lower Rewanui Member near the Paparoa Aerial workings, show TiO_2/Al_2O_3 values which equal or exceed that of the Morgan Seam output from Liverpool Mine, and in one case, exceeds the value for Paparoa Aerial Mine. In view of this evidence, an influence from reworked Morgan volcanic facies exhumed by uplift in early Rewanui time must be considered. However, it is difficult to apply this interpretation to some P_2O_5 and TiO_2-rich coals encountered by the Rapahoe Sector drillholes, particularly in the case of seams which lie far from the volcanic area, and are correlated with the upper Rewanui horizon. Similarly, some Pike River Member 4 coals, which lack evidence of volcanic influence, have high TiO_2/Al_2O_3 ratios and high P_2O_5 in ash.

If TiO_2/Al_2O_3 ratios are tabulated for Rapahoe sector seams, a gradual increase in this ratio with depth can be demonstrated for most holes where multi-seam sections were encountered in the Rewanui Member (Table 6.5). This effect is unlikely to be related to source variation and probably reflects a gradual change in swamp character in response to increasing "maturity" of the Rewanui environment and rise in base level within individual areas.

Drillhole	Seam	Approx. depth (m)	TiO_2/Al_2O_3
622	4	280	0.046
"	3	292	0.053
"	2	316	0.076
"	1	325	0.112
623	4	46	0.048
"	3	88	0.051
"	2	124	0.042
"	1	178	0.064
624	4	97	0.098
"	3	163	0.091
"	2	170	0.126
"	1	227	0.160
626	4	358	0.111
"	3	362	0.118
"	2	366	0.118
"	1	379	0.132
630	4	135	0.049
"	3	222	0.066
"	2	241	0.061
"	1	285	0.151

Table 6.5 TiO_2/Al_2O_3 ratios for Rewanui Member seams in individual drillholes, Rapahoe Sector.

6.4.5 Distribution of Carbonate Minerals.

Siderite, dolomite, and calcite are common minerals in Paparoa coals. Analyses suggest that these minerals may be less abundant at Pike River, although this remains uncertain until mining or drilling provides fresh coal. Calcite and dolomite are considered to be epigenetic, occurring in cleats and fractures, whereas siderite occurs as syngenetic nodules (see Chapter 3). Both calculated and observed assemblages show that siderite is the dominant carbonate mineral in Paparoa coal.

At Greymouth, distribution of siderite within seams, and comparative abundance between seams from different members, has no obvious explanation. On available evidence, both Rewanui and Dunollie coals appear more siderite-rich than coals from the Morgan Member. Siderite is common in the matrix of sandstones from all three members (Smale, 1978), and particularly abundant in coarse sandstones and conglomerates of the Dunollie Member where it can be seen replacing matrix and altered feldspar.

Field observations of siderite in coal suggest that thin seams in sandstone-dominated sequences contain the highest concentrations of siderite, and abundant siderite has been noted in seams situated at the top of the Rewanui Member, where Goldlight Mudstone lies within a few metres of the seam roof. The mean percentage of siderite in computed mineral assemblages for run-of-mine coals (Table 4.4) shows Strongman Mine samples to have twice the amount present in Liverpool coals.

Siderite formation in coal is considered to occur as a result of CO_2 release by anaerobic fermentation in the peat (Irwin et al., 1977), or by thermal decarboxylation during the brown coal stage at burial depths generally much less than 500 m (Matsumoto and Iijima, 1981). More recently, isotopic data have been used by Botz et al., (1986) to show that nodular siderite in an Australian coal was formed during early diagenesis in response to anaerobic fermentation.

Apart from petrographic evidence of a pre-compaction origin, there is little indication of the time or depth of siderite formation in the Paparoa coals. However, siderite in the Dunollie Member coal clearly

predates the influx of marine-influenced groundwater which accompanied or followed deposition of the earliest marine sediments, which now lie some 30-60 m above the Dunollie seams.

In view of the known systematic variation of siderite composition with depth, particularly with respect to the Mn/Fe ratio (Curtis and Coleman, 1986), the observed correlation for these elements in Greymouth Paparoa coals (Chapter 5) suggests that siderite formed in a single, and probably short-lived, episode for each horizon.

A high activity of bicarbonate ion is believed to be responsible for the leaching and mobility of ferrous iron (Curtis and Spears, 1968). A major factor controlling access of iron to growth sites within the coal (or peat) is almost certainly the rate of pore fluid transport. Abundant siderite within coarse sandstones and conglomerates could be attributed to the greater permeability of these lithologies, and this control may explain the abundance of siderite in Rewanui Member coals. Sideritic enrichment of seams beneath the Goldlight Mudstone may reflect concentration of fluid flow at a permeability boundary.

Siderite growth in coal proceeds at least partly by replacement of macerals, but there is no clear evidence of siderite replacement of mineral matter in Paparoa coals, although a small amount of iron will be leached from mineral matter by bicarbonate activity. Therefore, environmental reconstruction, and other reasoning based on total ash values as a measure of detrital sediment, should incorporate a recalculation to eliminate the effect of Fe_2O_3 introduced by siderite occurrence.

6.4.6 Distribution of Sulphide Minerals

Significant amounts of pyrite and marcasite are found in some Greymouth Paparoa coals where the total sulphur content is elevated above a "background" of around 0.3% (sections 3.8, 5.4). From drill logs and coal analyses, it can be seen that coals showing these effects are almost entirely restricted to the Dunollie Member, and to the Rewanui Member in the western part of the coalfield where much thinner coal-measure sequences overlie the Rewanui seams. Furthermore, the Paparoa sequence above the western Rewanui seams consists chiefly of sands and

conglomerates of the Rewanui and Dunollie Members, with little or no Goldlight Mudstone present.

As argued by Wellman (1952) and Suggate (1959), ingress of sulphur-bearing solutions from the marine sediments overlying the Paparoa sequence appears to be the best interpretation of sulphur enrichment in Paparoa coals. These authors based their observations on enrichment within Dunollie Member coals, because little was known of the western Rewanui Member seams at that time.

The sulphides occur both in fractures and cleats, and by replacement of siderite (Figure 3.7). Alteration of siderite to pyrite has been confirmed experimentally by Smythe (1966), who used sulphide solutions to effect the conversion. It is not known whether the pyritisation of Paparoa siderite took place in response to transport of sulphide solutions, or whether deep circulation of marine water took place, allowing direct reduction of sulphates.

6.4.7 Distribution of Nickel.

The trend shown by nickel in ash from the sink-float fractions is one of distinctly organic association. This behaviour is consistent with the known organic affinity of nickel, which is readily absorbed on peat by cation exchange (Altekar et al., 1974), and subsequently forms organometallic complexes with hydrocarbon groups during organic maturation (Rankama and Sahama, 1950; Hodgson, 1954). Therefore, nickel concentrations should be compared on a whole-coal basis.

Nickel values are available only for coals analysed by the writer. Values range from less than 1 ppm to more than 160 ppm nickel in whole coal, but few distribution trends can be recognised. Nickel concentrations in the Morgan coals analysed are generally similar to those in Rewanui coals. Similarly, Pike River Member 3 seams as a group are not obviously more nickel-rich than Member 4 seams, although the highest value recorded (162 ppm Ni in whole coal) is from a basal seam resting directly on tuffs. Spot and narrow ply analyses show a large fluctuation in nickel values, indicating a non-uniform distribution within seams.

Nickel is typically concentrated in Paparoa coal ash as a result of the strong organic association of this element, whereas intra-seam sediments are depleted in nickel relative to the mudstones (Table 6.3). Factors other than source rock composition appear to be a dominant control on nickel distribution within and between seams; these aspects are discussed further in the following section.

6.5 FURTHER EVIDENCE FROM SERIAL PLIES, DRILLHOLES 628 AND 633

6.5.1 Introduction

Greymouth Drillholes 628 and 633, which are located some 2 km apart in the southern part of the Rewanui Sector, both encountered a thick seam (>10 m) near the base of a relatively thin upper Rewanui sequence resting on basement (Figures 4.4, 6.14). The spacing of the drillholes is too great to permit reliable interpretation of the intersections as a continuous seam. Newman (1985a) interpreted these two intersections as examples of highly contrasting swamp types, on the basis of petrographic character and other properties observed for whole-seam composites. The seam at DH 628 was assigned a type category II, whereas the coal in DH 633 was described as type category III (Table 6.6, see also section 6.3).

Although the seams in both drillholes are considered to be of similar rank (i.e., thermal maturity), on the basis of rank trends defined by coal in other drillholes in the vicinity, they differ substantially in volatile matter yield and vitrinite reflectance. It has been clearly shown, by analysis of serial plies, that some West Coast coals exhibit substantial isorank variability in these properties (J. Newman, 1985a, 1987). Petrographic differences between the seams in Drillholes 633 and 628, in terms of principal maceral groups, are relatively high for West Coast coals. The DH 628 seam contains 12% inertinite in comparison to 3% for the DH 633 example. However, differences in vitrinite character, as indicated by the differing reflectance values, are seen to be the chief cause of the contrasting volatile matter values. Swamp conditions for the DH 633 seam are inferred to have been poorly oxygenated as a result of a persistently high water table, leading to the preservation of a more

Drillhole			628	633
Seam			1	1
CRA No.			26/376	26/662
Seam thickness (m)			10.65	10.3
Metres below top of Rewanui			36	12
Proximate Analyses Air-dried	Moisture	%	9.9	9.3
	Ash	%	3.2	5.8
	Volatile Matter	%	37.2	41.8
	Fixed carbon	%	49.7	43.1
Calorific value	MJ/Kg		29.14	28.2
	Btu/lb		12530	12120
Sulphur		%	0.29	0.59
Crucible swelling index			1	1
$dmm\frac{1}{2}sf$ basis	Volatile matter	%	42.4	48.8
	Vitrinite	%	79	84
	Resinite	%	1	2
	Sporinite	%	4	5
	Cutinite	%	-	2
	Fusinite	%	2	tr
	Semifusinite	%	7	1
	Macrinite	%	-	-
	Sclerotinite	%	tr	-
	Micrinite	%	tr	-
	Inertodetrinite	%	3	2
	Mineral matter	%	4	4
	Total vitrinite	%	79	84
	Total exinite	%	5	9
	Total inertinite	%	12	3
	$\bar{R}o$ max	%	0.54	0.38
Type category assigned (I to IV)			II	III

Table 6.6 -Seam location, stratigraphic position, thickness, some physical and chemical analyses, maceral analyses, and vitrinite reflectance for the main Rewanui seam in Drillholes 628 and 633, Rapahoe Sector. Type categories are assigned on the basis of coal petrography and volatile matter yield. Correction of volatile matter to a dry, mineral matter and half sulphur free basis ($dmm\frac{1}{2}sf$) is discussed in Chapter 8.

anoxic peat, and ultimately, a more perhydrous coal (Newman and Newman, 1982). In contrast, the DH 628 swamp is inferred to have been more emergent and better oxygenated, with periodic dehydration of the surface peat.

In view of the contrasting petrographic character of these coals, and the division into a large number of plies, each seam has been studied in detail by analysing the full set of serial plies. Graphic logs, compiled from the geologist's drill log, are shown as columns for each seam in Figures 6.15 and 6.16. Accompanying the columns are profiles for ash, P_2O_5 and strontium in ash, and Na_2O and Ni on a whole-coal basis.

Ash constituents analyses for the two ply sets are shown in Table 6.7, and computed mineral assemblages in Table 6.8. These data have been incorporated in many of the graphs appearing in Chapters 5 and 6, with the points identified to allow a comparison between the two profiles, and a comparison with whole seam composites from other Rapahoe Sector drillholes.

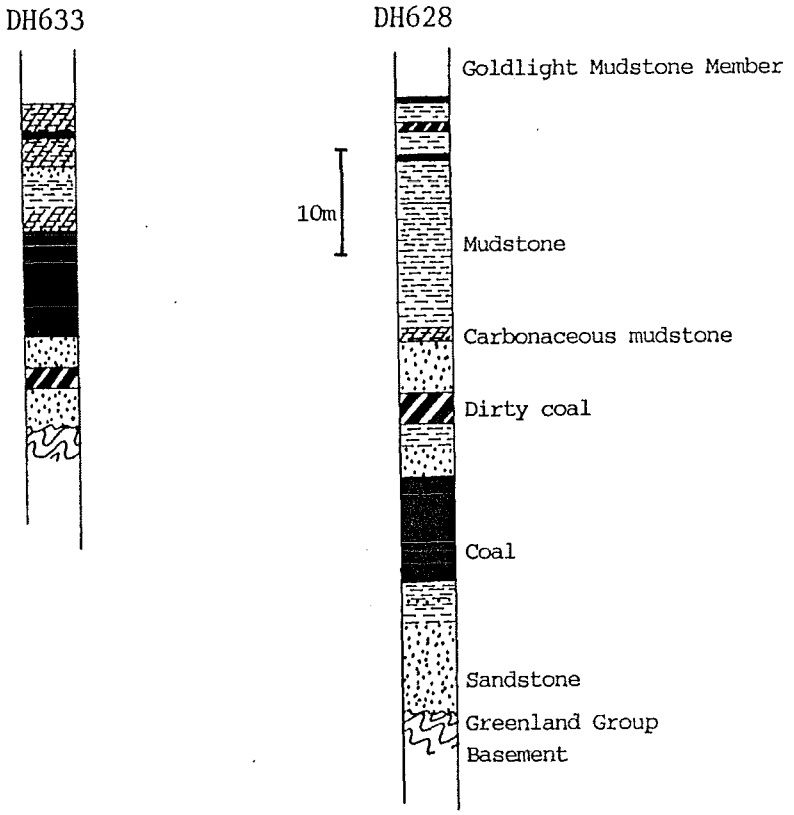


Figure 6.14 Simplified stratigraphic columns for Rewanui Member, Drillholes 633 and 628, (Rapahoe Sector, Greymouth Coalfield).

6.5.2 Ash, SiO_2, and Al_2O_3

The thick seams in Drillholes 628 and 633 are both low ash. Figure 6.15 shows the DH 628 seam to be consistently low ash throughout, with the exception of three thin silt horizons which together comprise more than half the total mineral matter in the full seam thickness. If those bands are excluded, the average ash yield is approximately 1.7%, and an even smaller value is obtained if a correction is made for authigenic siderite. The DH 628 swamp is envisaged to have existed in a stable environment where it received minimal suspended sediment except during three brief periods of flooding. In contrast, the seam in DH 633 is clearly more mineral matter-rich (Figure 6.16). The lower part of the seam shows a gradual change from high ash to low ash, but the ash value does not fall to the very low levels which characterise the seam in DH 628. The upper part of the DH 633 seam contains approximately 1 m of carbonaceous mudstone which is not represented in the plies because of core loss. "Chuckie stones" are noted in the log at several horizons, and probably contribute a significant proportion of the total ash.

Ply analyses from these seams show distinct trends when plotted on an Al_2O_3/SiO_2 diagram (Figure 6.17). With the exception of a quartz-rich roof ply and silty bands, DH 628 samples show a strongly aluminous bias, whereas most of the DH 633 samples are clearly dominated by quartz. The distinction is also well illustrated by the quartz-kaolinite-illite variation diagram for Rapahoe Sector samples (Figure 6.9) which shows the plies from each drillhole occupying extreme opposite positions within the field.

It is notable that both sets of plies are comparatively low in illite. If the effect of rafted grains and "chuckie stones" were removed from the analyses, both seams should show a kaolinitic composition, and the contrast in ash values would decline.

Sample	Drillhole/Ply	M%ad	A%ad	S%ad	MgO	Na2O	SiO2	Al2O3	SO3	P2O5	Fe2O3	MnO	TiO2	CaO	K2O	Sr(ppm)	Ni(ppm)
26/359	628/1PLY1	8.2	4.4	0.3	0.36	0.65	82.27	9.28	0.45	0.04	4.27	0.06	1.80	0.64	0.11	104	1272
26/360	628/1PLY2	9.9	3.9	0.3	5.50	0.77	19.15	6.81	0.79	0.08	63.93	0.39	0.46	0.86	0.06	60	978
26/361	628/1PLY3	10.1	2.4	0.3	1.93	1.24	45.86	14.69	0.91	0.53	29.58	0.21	2.34	1.45	0.20	456	1157
26/362	628/1PLY4	7.7	23.8	0.3	0.28	0.00	63.80	15.42	0.69	4.20	0.88	0.01	9.44	1.71	0.87	4060	53
26/363	628/1PLY5	9.5	2.2	0.3	3.09	1.34	31.63	20.97	1.36	3.05	33.52	0.29	0.85	5.19	0.21	1213	531
26/364	628/1PLY6	10.2	0.8	0.3	1.12	4.68	55.41	22.87	0.73	0.34	8.45	0.05	1.56	2.15	0.34	350	307
26/365	628/1PLY7	10.0	1.3	0.3	5.23	4.12	28.94	13.49	3.50	0.14	38.28	0.25	0.77	2.83	0.39	255	96
26/366	628/1PLY8	10.5	0.9	0.3	3.19	4.07	40.35	27.19	1.13	0.09	22.56	0.16	0.90	2.17	0.27	326	148
26/367	628/1PLY9	7.8	16.6	0.3	0.79	0.25	66.59	24.11	0.00	0.30	1.30	0.00	0.90	0.18	4.70	600	0
26/368	628/1PLY10	9.7	2.5	0.4	0.82	2.59	56.17	30.81	0.26	0.16	4.04	0.00	1.00	1.02	2.37	312	69
26/369	628/1PLY11	10.0	1.2	0.4	1.27	4.30	51.43	28.76	0.60	0.14	7.55	0.05	1.28	1.87	0.82	295	77
26/370	628/1PLY12	9.9	1.2	0.4	2.17	3.24	48.66	26.08	1.04	0.16	12.14	0.04	1.40	1.95	1.43	394	98
26/371	628/1PLY13	10.4	1.6	0.3	5.54	4.44	32.04	16.97	2.79	0.10	32.31	0.21	1.02	3.34	0.34	161	67
26/372	628/1PLY14	10.5	0.8	0.3	1.12	5.60	49.54	28.62	1.99	0.09	9.00	0.05	1.40	1.69	0.54	338	353
26/373	628/1PLY15	9.8	1.0	0.4	0.57	4.14	52.39	32.67	0.39	0.08	2.91	0.00	2.56	1.46	0.67	298	1037
26/374	628/1PLY16	3.8	56.4	0.3	0.91	0.10	66.97	25.00	0.06	0.71	2.66	0.02	0.75	0.83	3.89	458	29
26/375	628/1PLY17	9.5	4.7	0.4	0.99	1.85	57.83	28.09	0.54	1.18	1.62	0.02	1.83	1.07	1.53	2164	1383
26/647	633/1PLY1	8.4	22.5	2.2	0.40	0.49	76.00	10.03	0.20	0.04	9.55	0.01	1.22	0.33	1.60	125	72
26/648	633/1PLY2	10.0	2.6	1.0	0.24	2.14	65.40	8.99	2.08	0.03	17.23	0.01	1.51	1.36	0.30	474	261
26/649	633/1PLY3	9.7	2.8	0.4	7.75	3.05	29.58	9.45	8.02	0.13	35.48	0.16	0.59	5.15	0.31	673	353
26/650	633/1PLY4	9.8	7.3	0.6	0.20	1.65	86.45	4.62	1.06	0.03	4.08	0.01	0.94	0.93	0.09	302	89
26/651	633/1PLY5	10.2	3.7	0.5	0.36	3.70	67.79	11.23	2.86	0.03	9.66	0.03	1.16	2.03	0.18	651	195
26/652	633/1PLY6	9.7	2.5	0.8	0.66	5.05	47.07	14.66	6.96	0.03	18.44	0.00	1.05	3.35	0.52	1016	202
26/653	633/1PLY7	9.3	2.0	0.7	0.69	5.43	41.60	13.93	7.61	0.05	22.26	0.01	0.89	3.69	0.45	948	132
26/654	633/1PLY8	9.3	4.8	0.7	0.36	3.42	71.49	13.85	1.63	0.03	6.02	0.03	1.35	1.95	0.35	594	93
26/655	633/1PLY9	10.1	3.4	0.8	0.40	3.63	58.09	15.08	3.31	0.04	14.29	0.00	1.00	2.09	0.34	655	123
26/656	633/1PLY10	9.6	4.5	0.9	0.32	2.37	62.11	9.77	2.56	0.03	19.04	0.00	1.06	1.56	0.23	474	97
26/657	633/1PLY11	10.2	4.6	1.0	0.24	2.62	59.55	15.42	2.14	0.03	17.60	0.00	0.86	1.41	0.17	420	97
26/658	633/1PLY12	9.0	4.5	0.7	0.35	2.22	63.70	13.89	2.53	0.03	14.14	0.03	1.07	1.61	0.14	490	125
26/659	633/1PLY13	9.6	4.9	0.8	0.32	2.69	60.23	16.67	2.80	0.03	13.80	0.00	0.94	1.79	0.17	601	140
26/660	633/1PLY14	8.1	9.9	0.7	0.17	1.18	77.75	11.76	0.59	0.40	4.49	0.02	1.22	0.85	0.25	942	66
26/661	633/1PLY15	8.3	20.7	0.6	0.21	0.44	82.70	10.75	0.16	0.22	2.28	0.01	1.15	0.35	0.49	482	54

Table 6.7 Ash constituent analyses for serial plies from Rewanui Member thick seams in Drillholes 628 and 633, Greymouth Coalfield.

Table 6.8 Computed mineral assemblages for serial plies, Drillholes 628 & 633, Greymouth Coalfield.

Sample	DH/Ply	A%	Qtz	Kaolin.	Illite	Rutile	Sid.	Cal.	Crand.	Pyrite	MM/A
26/359	628/1	4.4	70.3	18.9	1.2	1.8	7.7	0.0	0.1	0.0	1.05
26/360	628/2	3.9	8.4	10.6	0.5	0.3	80.0	0.0	0.2	0.0	1.37
26/361	628/3	2.4	25.6	25.5	2.0	2.1	43.5	0.0	1.4	0.0	1.20
26/362	628/4	23.8	50.5	16.0	9.7	9.5	2.0	0.0	12.3	0.0	1.05
26/363	628/5	2.2	8.8	30.3	1.9	0.7	50.9	0.0	7.4	0.0	1.27
26/364	628/6	0.8	29.3	47.2	3.9	1.6	16.6	0.5	1.0	0.0	1.13
26/365	628/7	1.3	11.1	22.1	3.7	0.7	62.0	0.0	0.4	0.0	1.26
26/366	628/8	0.9	7.3	50.4	2.7	0.8	38.6	0.0	0.2	0.0	1.22
26/367	628/9	16.6	33.7	10.5	50.6	0.9	3.5	0.0	0.8	0.0	1.06
26/368	628/10	2.5	18.1	45.8	26.2	1.0	8.2	0.2	0.5	0.0	1.11
26/369	628/11	1.2	17.3	56.0	9.3	1.3	15.3	0.5	0.4	0.0	1.14
26/370	628/12	1.2	16.5	42.7	15.4	1.4	23.6	0.0	0.5	0.0	1.15
26/371	628/13	1.6	10.3	29.3	3.3	0.9	56.0	0.0	0.3	0.0	1.25
26/372	628/14	0.8	15.8	58.8	6.1	1.4	17.5	0.1	0.3	0.0	1.13
26/373	628/15	1.0	14.0	68.1	7.8	2.7	6.2	1.0	0.2	0.0	1.12
26/374	628/16	56.4	33.1	17.7	40.6	0.7	5.9	0.1	1.9	0.0	1.08
26/375	628/17	4.7	25.7	46.2	17.5	1.9	4.9	0.3	3.5	0.0	1.10
26/647	633/1	22.5	59.7	7.4	16.9	1.2	1.4	0.2	0.1	13.1	1.01
26/648	633/2	2.6	51.9	16.1	3.2	1.4	0.0	2.8	0.1	24.6	0.56
26/649	633/3	2.8	16.0	15.4	3.0	0.5	63.7	0.0	0.3	1.1	1.23
26/650	633/4	7.3	81.3	9.2	1.0	0.9	2.3	0.7	0.1	4.4	1.01
26/651	633/5	3.7	55.8	23.4	2.1	1.2	10.9	1.0	0.1	5.6	1.04
26/652	633/6	2.5	30.6	28.5	6.0	1.1	5.8	3.0	0.1	24.8	0.98
26/653	633/7	2.0	26.1	27.6	5.2	0.9	12.3	2.7	0.2	25.0	0.99
26/654	633/8	4.8	54.6	26.9	3.9	1.3	0.0	4.2	0.1	9.0	1.02
26/655	633/9	3.4	40.5	30.1	3.8	1.0	3.6	1.8	0.1	19.1	1.01
26/656	633/10	4.5	48.6	18.5	2.5	1.0	11.9	0.3	0.1	17.1	1.02
26/657	633/11	4.6	39.6	30.7	1.8	0.8	5.0	0.8	0.1	21.1	1.02
26/658	633/12	4.5	46.2	28.4	1.5	1.0	12.0	0.3	0.1	10.4	1.05
26/659	633/13	4.9	40.0	34.4	1.9	0.9	6.5	1.1	0.1	15.1	1.03
26/660	633/14	9.9	64.4	22.6	2.8	1.2	2.6	0.5	1.2	4.7	1.04
26/661	633/15	20.7	70.0	18.7	5.5	1.2	2.8	0.0	0.6	1.3	1.04

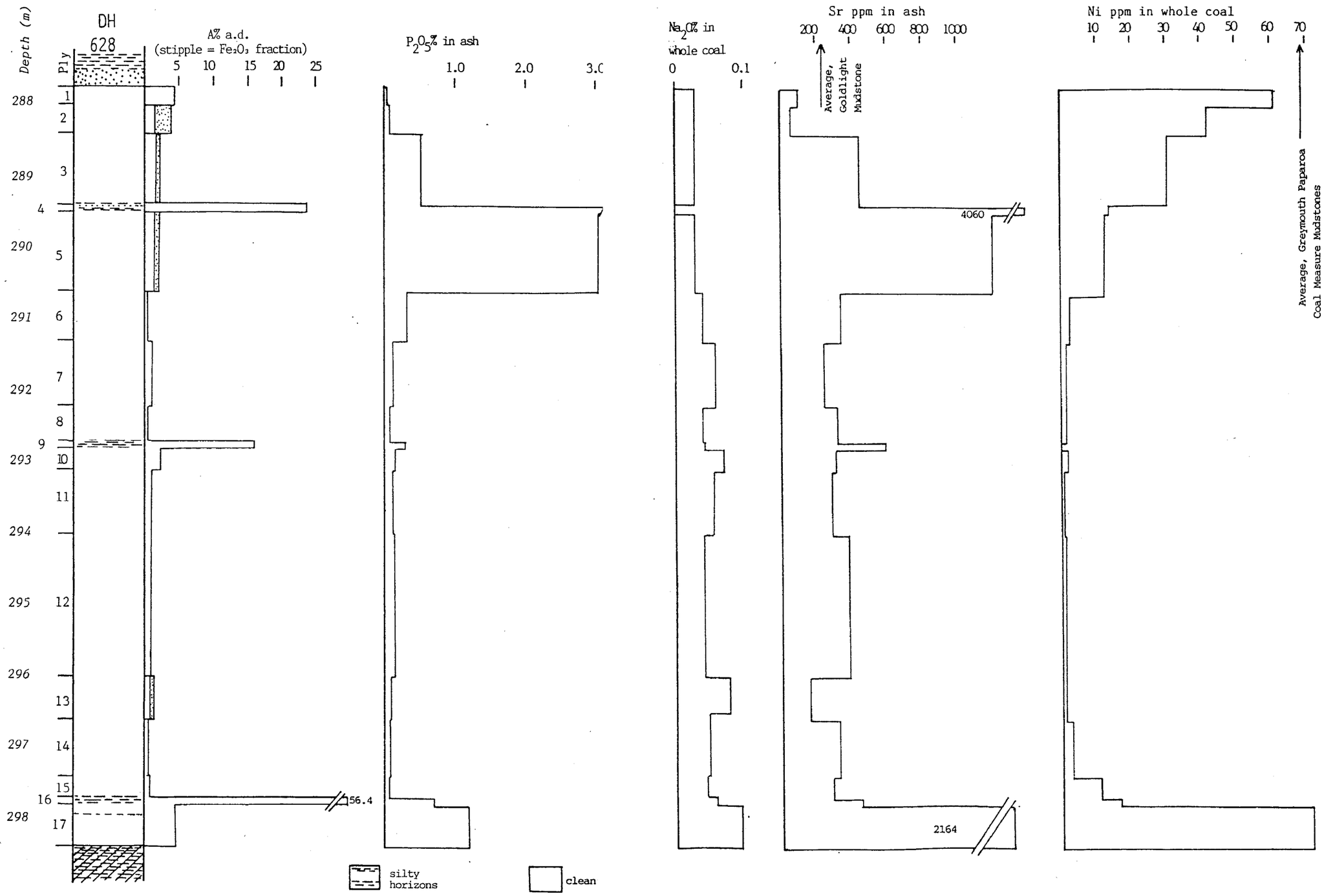


Figure 6.15 Graphic log and geochemical profiles for thick seam in nui Member, Greymouth Drillhole 628.

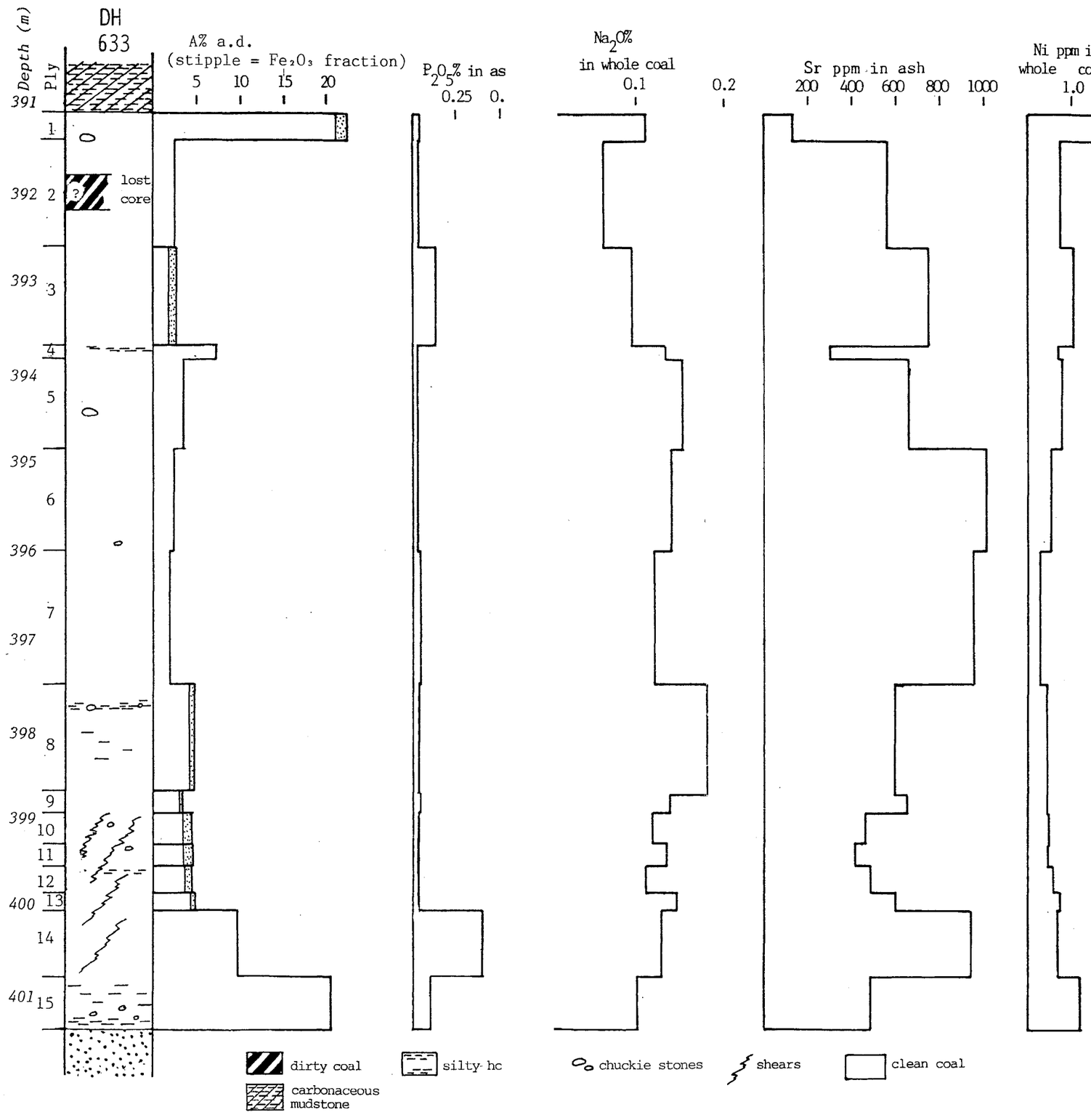


Figure 6.16 Graphic log and geochemical profiles f ick seam in the Rewanui Member, Greymouth Drillhole 633.

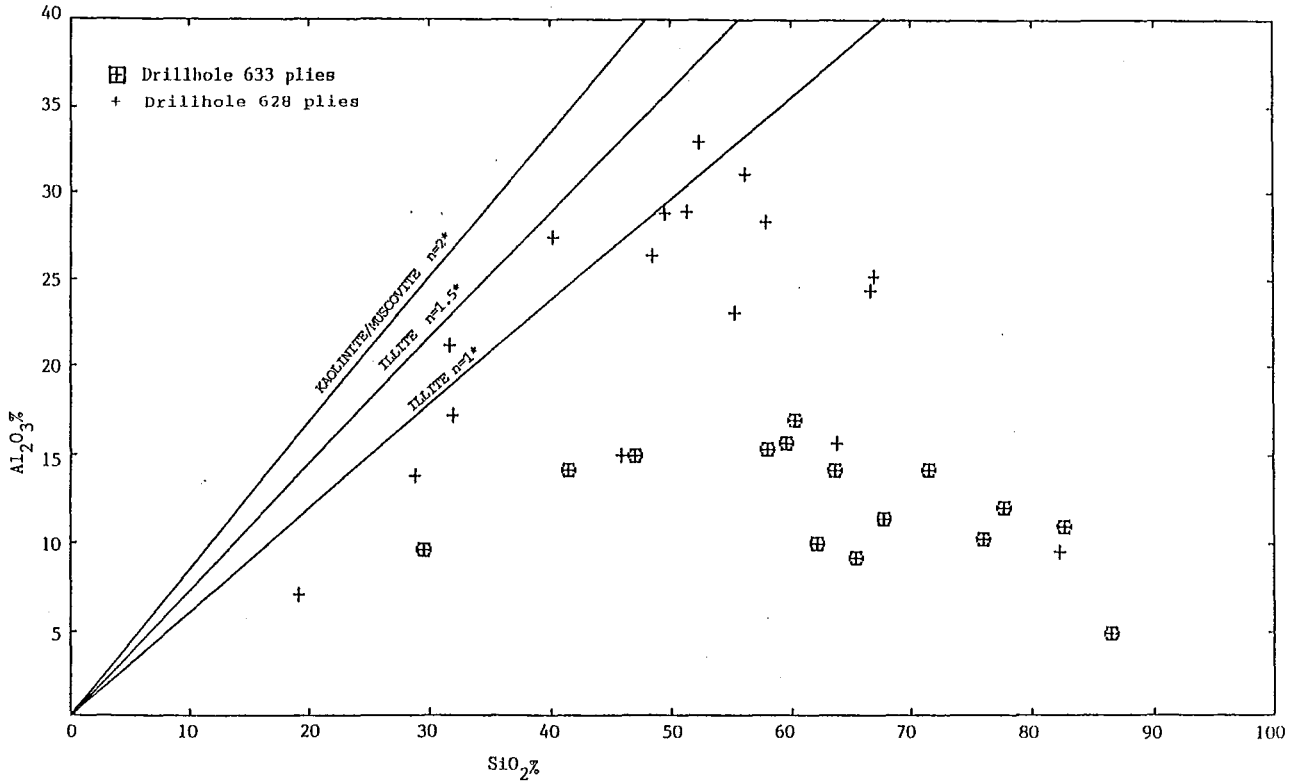


Figure 6.17 Al_2O_3 vs SiO_2 for plies from thick seams in Rapahoe Sector Drillholes 628 and 633.

6.5.3 P_2O_5 and Strontium.

Both seams contain extremely low "background" values of P_2O_5, although DH 628 has consistently higher values (note the difference in P_2O_5 scales in Figures 6.15 and 6.16). An extreme value of 4.2% P_2O_5 in ash is found in the uppermost silty band in the DH 628 seam (ply 4), and coal plies above and below this band are also phosphorus-enriched.

A volcanic or chemical origin for ply 4 is incompatible with the character of the mineral matter. Microscopic examination of LTA from this ply reveals a mixture of fine-grained clay, accompanied by angular to subrounded quartz grains which exhibit solution textures. If this band can be regarded as detrital sediment, phosphorus enrichment of this material could be a result of one or more of the following effects:

(i) Influx of a phosphatic sediment from soil horizons surrounding the swamp.

(ii) Concentration of crandallite, as an insoluble residue, by loss of mineral matter and oxidation of organic matter, at the peat surface.

(iii) Intense or prolonged fixation of phosphate by reaction with Al and Ca species.

The silty band contrasts sharply with the very low ash coal above and below, and can be considered to represent a very rare flooding episode; it is difficult to envisage introduction of such large amounts of phosphorus in a single event. Petrographically, ply 4 is generally similar to the average seam type, and shows no evidence of advanced oxidation.

Phosphate enrichment of plies beneath ply 4 suggests a crandallite origin involving mobile phosphate within the swamp. Following deposition of the sediment at the ply 4 horizon, a period of leaching may have supplied the adjacent peat with a very substantial increase in dissolved aluminium, leading to fixation of phosphorus as insoluble crandallite.

Episodes of dessication may have been sufficiently intense to decompose the uppermost layers of peat, including the actively growing plants, thereby releasing a relatively large quantity of soluble phosphate.

Ply 4 clearly differs from the silty bands at plies 9 and 16, which are not significantly P_2O_5-enriched, suggesting that special environmental conditions accompanied or followed deposition of the uppermost band. However, conditions favouring phosphorus fixation may also have existed when the peat first accumulated at the DH 628 locality, as shown by moderate P_2O_5 values for the basal ply; proximity to the floor, and possibly the nearby silt band (ply 16), may have contributed to higher concentrations of phosphate, dissolved aluminium, or both.

Distribution of crandallite in the DH 628 seam is well illustrated by the strontium profile, which closely follows the P_2O_5 variation. In contrast, strontium in the DH 633 seam shows no relationship to the low and uniform levels of P_2O_5 in ash, but can be shown to be occurring in calcite (Figures 6.16, 5.15). An antipathetic relationship of strontium with ash suggests that the calcite is very evenly distributed, thereby emulating an organic association.

6.5.4 Na_2O

Because sodium in coal exhibits a strong organic association, Na_2O has been profiled on a whole-coal basis in Figures 6.15 and 6.16. The concentration in the DH 628 seam is generally low, but shows a broadly inverse relationship with P_2O_5 and strontium. The crandallite-rich ply 4 contains undetectable Na_2O (< 0.1% in ash), in contrast to the other high-ash bands. In DH 633 coal, Na_2O values are much higher; no clear relationship with P_2O_5 or strontium can be seen, and evidence previously discussed suggests that sodium values in this coal are unrelated to clays (Section 5.7). A graph of Na_2O in ash against reciprocal of ash demonstrates a major distinction between these two seams (Figure 6.18); the DH 633 coal shows consistently high values which plot as extremes for the Rapahoe Sector samples as a whole, whereas the DH 628 values are lower and much more variable. The DH 628 samples could be divided into a "uniform" group, comprising most of the upper plies, and an "enriched" group, which show higher Na_2O-in-coal values.

However, there is no obvious interpretation for either the differences between the two seams, or the variability within individual seams. Both seam profiles show insignificant sodium contribution from included sediment, conforming to the general observation that all sediments associated with the Paparoa coals are strongly depleted in sodium, as are the lacustrine mudstones themselves. Therefore, sodium content and distribution within the coals must be attributed to cation exchange, and can be expected to fluctuate in response to groundwater composition thoughout the peat and lignite stages of maturity (Miller and Given, 1986). During this period, sodium must compete with other cations for exchange sites, and tends to be desorped by divalent and trivalent cations (e.g., Fowkes, 1978; Miller and Given, 1986).

In view of these constraints, two possible factors controlling sodium in the coal can be proposed:

(i) An abundance of Al^{3+} in the DH 628 seam may have persisted over a very long period, inhibiting Na^{+} adsorption. Supply of abundant Al^{3+} within the upper plies, particularly near the crandallitic, high ash ply 4, may explain the lower sodium-in-coal values for that part of the seam. The coincidence of extremely low sodium with

ply 4 is particularly notable in this respect.
However, such a control appears unlikely for other aluminous coals; sample 27/531 (Pike River), and several boehmite-bearing Brunner coals contain high values of sodium, which occurs as dawsonite.

(ii) From the evidence of pyritic alteration of siderite, and elevation of sulphur content, the more sodium-rich DH 633 profile might be considered to have inherited sodium from marine-influenced groundwater, after burial to some 200-300 m. It is not clear whether this effect has introduced sodium into the coals; the Tiller Mine sample (Dunollie Member) shows no sign of elevated sodium, despite a close proximity to the marine source, and extensive pyritic alteration of siderite. Furthermore, some relatively sodium-rich Paparoa coals in the centre and east of the Greymouth Coalfield show no sign of influence from marine sources.

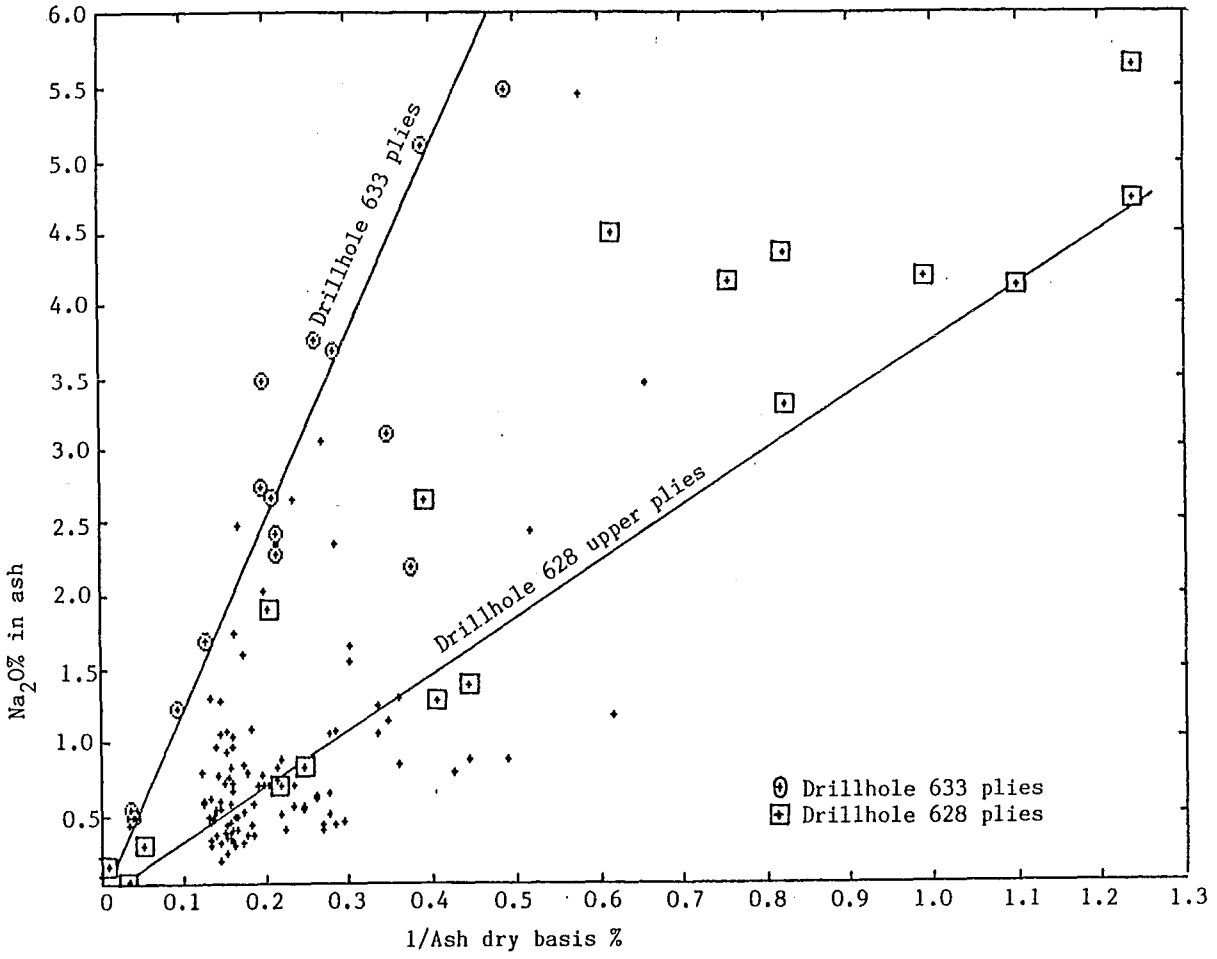


Figure 6.18 Na_2O in ash vs reciprocal of ash for all Rapahoe Sector samples, showing plies for drillholes 628 and 633.

6.5.5 Nickel.

The profile of nickel in whole coal for the DH 628 seam shows extremely low values mid-seam, rising sharply at roof and floor to values similar to the mudstone average. This pattern is remarkably similar to the trends of postdepositional sulphur enrichment in seams from the Brunner Coal Measures (e.g., Newman, 1985a). By analogy, nickel in the DH 628 seam is considered to have been introduced by groundwater after burial; nickel enrichment of this type has been reported from overseas coals by Nicholls (1965). A similar pattern exists for the DH 633 seam, although the rise at roof and floor is much smaller, and the overall pattern is less well defined.

Trends in nickel distribution inherited from the swamp appear to be absent, or completely overprinted by post-burial enrichment. Furthermore, nickel distribution shows no relationship with the other groundwater-introduced components, siderite and sulphur.

It is difficult to explain the differences in nickel distribution in the two seam sections, Enrichment involving cation exchange at the brown coal stage is envisaged, because seam permeability declines rapidly as coalification advances.

Very low mid-seam nickel values for the DH 628 profile in comparison to that of DH 633 may be related to occupation of exchange sites by ionic aluminium during early coalification.

6.5.6 Statistical Comparison of Type Classes

Contrasting mineralogical and geochemical features for the seams in DH 628 and DH 633 are summarised in Table 6.9. A combination of these features may be useful in distinguishing seam types as determined by swamp character, but obviously further testing is required. The data suggest that these two seams represent extreme and opposite end-members of a series which probably includes intermediate and mixed swamp types.

Table 6.10 summarises computed quartz-kaolinite-illite, crandallite, and sodium in whole coal for all Rapahoe Sector Rewanui coals which were assigned a type category by J. Newman (1985a, 1987). Overall, distinctive separation of these type categories appears poor, due to the large standard deviations present. Many of the type category assignments are shown by Newman to be uncertain, or to be mixtures of two categories. Much of this uncertainty may be resolved if petrographic analysis of plies were undertaken.

However, several complicating factors controlling mineral matter may be present, particularly with respect to crandallite. Newman's single representative of type category IV, which is envisaged as a deep water accumulation of transported plant fragments, contains an extreme abundance of crandallite and little quartz. Crandallite development in this environment is inconsistent with the foregoing observations of crandallite origin, and it is tentatively suggested that this mineral has been transported from the surface of surrounding, emergent swamps, together with the partly oxidised plant debris.

Table 6.9 Summary of mineralogical and geochemical differences between thick seams intersected in Greymouth Drillholes 628 and 633.

	Drillhole 628	Drillhole 633
Quartz)	low, variable	high (rafted origin)
Kaolinite) 100%	high, variable	depressed by rafted quartz
Illite)	low, variable	low
Crandallite	high, associated with sediment	low-absent
Sr	present in crandallite	present in carbonates
Ni "background"	very low	low-intermediate
Ni "enrichment" (roof, floor)	high	low
Na_2O (whole coal)	low, variable	high, uniform

Table 6.10 Mineralogical comparison of seam composites of different type classes assigned by Newman (1985a). Figures in brackets represent standard deviations.

	No. of samples	Base 100%			Crandallite	Whole coal Na_2O
		Quartz	Kaolinite	Illite		
Type Category I	14	45(13)	35(12)	19(10)	0.7(0.5)	0.029(0.016)
Type Category II	8	52(10)	29(5)	20(10)	1.4(2.5)	0.054(0.042)
Type Category III	6	51(15)	36(6)	12(12)	1.2(1.6)	0.086(0.027)
Type Category IV	1	21	55	24	16.1	0.036

6.6 SUMMARY

Coals of the Paparoa Coal Measures can be seen to represent a wide range of mineralogical and geochemical character. Paparoa Coal Measure mudstones, in contrast, have a very uniform composition and provide an example of the fine sediment which entered the low ash peat swamps. Comparison of mudstone and ash chemistry reveals the compositional and mineralogical alteration which has taken place in the swamp after deposition. In the case of Paparoa coals, little variation in ash chemistry can be attributed to source rock composition, whereas paleoenvironmental differences are considered to exert a major control. Two end-member regimes can be independantly distinguished on the grounds of geochemical and coal type studies:

(i) Coals inferred to have resulted from high water table swamps (Newman, 1985a), characterised by abundant quartz relative to illite and kaolinite. Some of the excess quartz may be authigenic, but most is considered to have been rafted into place on floating vegetation during flood episodes. A persistently high water table and relatively restricted drainage has limited the intensity of silicate leaching at the peat surface, and highly aluminous minerals such as boehmite and dawsonite are absent. Crandallite is sparse, and sodium-in-coal values are relatively high.

(ii) Coals inferred to have resulted from relatively low water table swamps (Newman, 1985a). Good drainage (6.3) and periodic aeration of the peat surface is believed to have promoted silicate leaching and kaolinite formation. The resulting coals are typically kaolinite-rich and quartz-poor, and some contain traces of boehmite and dawsonite in low-ash fractions. Crandallite can be relatively abundant, and sodium-in-coal values relatively low except where dawsonite is present.

The thick Rewanui Member seam in DH 633 represents an extreme example of a high water table swamp, whereas the seam at DH 628 offers a major contrast, exhibiting evidence of a low water table swamp. A more extreme version of the low water table swamp environment is represented by seams of the Dunollie Member.

It is difficult to separate the effects of source and environment on the abundance and distribution of the minor components P_2O_5 and TiO_2. Environmental effects are probably dominant in determining local concentrations of both of these ash constituents. Only those seams which developed in very close proximity to volcanics can be considered to be definitely influenced by the volcanic lithology, e.g., Paparoa Aerial coal, and some Member 3 Pike River seams which have very high TiO_2 values.

The ratio TiO_2/Al_2O_3 may be broadly diagnostic of swamp water table levels, but local effects cause a wide fluctuation in this ratio.

Phosphorus, which may occur largely or entirely as crandallite, has an extremely non-uniform distribution. It is proposed that fixation of phosphate as crandallite occurs when an abundance of dissolved aluminium enters the peat; release of high concentrations of phosphate to groundwater during dessication may also be important.

Sodium-in-coal values appear to be generally higher in coals developed from high water table peats, but controls on the distribution of this element appear to be complex.

Siderite is abundant throughout the Paparoa coals at Greymouth Coalfield, but may be sparse at Pike River. The greatest abundance of siderite appears to coincide with coarse-grained sediments of the Rewanui Member, where permeability was greatest. Rewanui Member coals tend to be substantially more sideritic than Morgan Member coals. Seams of the Dunollie Member, and seams of the Rewanui Member in the west of Greymouth Coalfield, may contain sufficient pyrite and marcasite to substantially elevate total sulphur values. The sulphides occur chiefly by replacement of siderite.

Graphs of Al_2O_3/SiO_2, and ternary diagrams based on the relative proportions of total quartz, kaolinite, and illite, are useful for distinguishing gross paleoenvironmental characteristics, and calculation of mineral matter assemblages from ash constituents provides a useful means of comparing coals on a quantitative basis.

CHAPTER 7

CONTROLS ON MINERAL MATTER IN BRUNNER COALS

7.1 INTRODUCTION

The principal controls on mineral matter in Brunner coals can be defined as follows:

(i) Composition of sediments entering the swamps.

(ii) Peat swamp character (physiography, drainage, flora etc.)

(iii) Rate of peat accumulation, and extent of swamp duration.

(iv) Influence of marine water and marine sediment during peat accumulation.

(v) Circumstances of the marine transgression which terminated or followed peat accumulation.

Whereas the Paparoa coals are contained in two very similar sedimentary sequences which may have been part of a single depositional trough, Brunner coals occur in a number of widely scattered deposits of various ages, depositional settings, and differing source material (1.4.3). Therefore, it is not appropriate to treat analytical data for Brunner coals in the same way that has been adopted for Paparoa samples. In particular, it may be misleading to present analyses from different areas on common plots, except for comparative purposes, and no single lithology can be selected to represent the sedimentary influx to the peats.

A variety of locally derived source material occurs in sediments of the Brunner Coal Measures, although mainly Greenland Group and granitic lithologies are represented. The coal measure sediments are highly quartzose in many areas, reflecting very limited supply from low-relief source areas. In view of the extensive alteration of sediment which has taken place in some Brunner swamps (see below), the effect of sediment composition as a control on mineral matter is considered to be of minor importance. Very stable tectonic conditions during Brunner accumulation in some areas probably favoured exceptionally long-lived swamps,

although the extreme example at Greymouth Coalfield (pollen zone B to C, see 1.4.3) is probably unique to that area (Nathan et al., 1986). Extended periods of swamp duration can be expected to accentuate both degradation of macerals and leaching of inorganic material.

Very little paleoenvironmental analysis has been documented for Brunner Coal Measures on the West Coast. Studies have been carried out for small areas at Pike River and Buller Coalfields (Newman 1985a, 1986) and a major work encompassing most West Coast areas is currently in progress (Titheridge, in prep.). Evidence from different areas indicates that a wide range of sub-environments existed (back-barrier/ lagoonal to fluviodeltaic, and fluvial), but a common factor appears to be a marginal marine setting.

Brunner coals generally exhibit poor tissue preservation, and many are perhydrous in comparison to Paparoa coals of similar rank, although some high-moor Brunner coals have a notably low-volatile type. Inertinite is always very sparse, and is dominated by semifusinite, and to a lesser extent, sclerotinite. The origin of the distinctive petrographic character of Brunner coals is not completely understood. Tissue degradation to produce the observed predominance of desmocollinite, vitrodetrinite, and liptodetrinite has been attributed to both (i) anoxic degradation in relatively alkaline conditions, and (ii) wet but well-drained (hence relatively oxygenated) raised bog environments, which have jointly influenced peat accumulation in the areas studied. Both environments, for different reasons, are considered to have favoured bacterial decay of a floral assemblage which was probably dominated by soft-tissued plants (Newman, 1986).

The influence of brackish water on Brunner peats during accumulation is difficult to identify by geochemical means, particularly where a strong "overprint" is imposed by marine transgression following peat accumulation. On the basis of coal petrography and proximate analyses, Newman (1985a) considered that there was no evidence for syndepositional sulphur enrichment of Webb-Baynes coal (Buller Coalfield). However, some Brunner coals at Pike River Coalfield and in the Upper Waimangaroa Sector of Buller Coalfield are believed to originate from lagoonal swamps which were poorly drained and brackish. In these cases,

extreme pyrite enrichment near some seam roofs is tentatively attributed to direct exposure of peat to seawater after drowning of the swamps (Newman, 1985a, 1986).

Many Brunner seams are sulphur-enriched to some degree by infiltration of marine water via roof and floor sediments after burial, as originally proposed by Wellman (1952) and later discussed by Suggate (1959). Petrographic observations and analytical data strongly suggest that both pyritic and organic sulphur (e.g. Newman, 1986) increase as a result of this effect, which commonly enriches the upper and lower margins of Brunner seams. Lithological control of sulphur enrichment patterns is well known (e.g., Donaldson et al., 1980). Newman (1985a) shows variation of total sulphur in Webb-Baynes and some Pike River Brunner seams to be related to the permeability of enclosing sediment.

7.2 GREYMOUTH COALFIELD

7.2.1 Mineral Matter in Greymouth Brunner Coals

Mineral assemblages observed in Greymouth Brunner coals (Table 4.3) show a remarkably hyperaluminous trend. Quartz is either sparse or absent, highly crystalline kaolinite is abundant, and in the southeastern area of the coalfield boehmite is common throughout the seam and very abundant within restricted horizons.

The boehmite-rich area extends throughout the region of the Brunnerton group of mines, i.e., Brunner, Tyneside, Wallsend, Coal Pit Heath, Pig and Whistle, and Dobson Mines, none of which is now working (Figure 4.2). A highly unusual mineral matter assemblage is suggested by old ash analyses for coal from Wallsend and Dobson mines (Table 7.1), published by Gage (1952). These analyses apparently drew little comment, except for a brief reference by Hughson (1953) concerning the elevation of ash fusion temperature by high alumina values. Boehmite in these coals is commonly accompanied by dawsonite, which appears to be a result of the unusually aluminium-rich environment within the coal.

Table 7.1 Ash analyses for Greymouth Brunner run-of-mine coals. Adapted from Gage (1952, Table XXII)

Coal Horizon	Brunner Horizon.			
Name of Mine	Wallsend.	Wallsend.	Dobson.	Dobson.
Mine No.	M. 2.	M. 2.	M. 44.	M. 44.
Sample No.	C.S. 218.	H. 3407/2.	C.S. 211.	H. 3407/1.
Percentage of Ash in Coal	9·1.	9·6.	5·6.	7·2.
Ash Analysis				
Silica	26·20	25·17	15·84	29·29
Titanium oxide	1·44	0·81	0·66	1·27
Alumina	33·09	22·57	24·20	29·73
Iron oxide	1·21	3·44	3·10	3·70
Manganese oxide	0·05	0·06	0·06	0·06
Magnesium oxide	4·20	4·23	7·39	3·17
Calcium oxide	15·29	22·20	25·33	15·30
Sodium oxide	1·33	1·25	1·34	1·08
Potassium oxide	1·28	0·52	0·64	1·32
Phosphate	0·37	0·54	0·17	0·47
Loss below 110° C.	0·36	0·18	nil	0·17
Loss above 110° C.	2·82	n.d.	1·99	n.d.
Carbon dioxide	n.d.	n.d.	n.d.	n.d.
Zirconium oxide	n.d.	n.d.	n.d.	n.d.
Sulphate	12·32	18·34	19·40	15·32
Chromium oxide	0·03	0·02	0·01	0·03
Vanadium oxide	n.d.	n.d.	n.d.	n.d.
Barium oxide	0·08	0·09	0·05	0·08
Boron oxide	tr.	n.d.	tr.	n.d.
Chloride	n.d.	n.d.	n.d.	n.d.
Strontium oxide	n.d.	n.d.	n.d.	n.d.
Total	100·07	99·42	100·18	100·99

NOTE.—n.d. = not determined. tr. = trace.

Al_2O_3/SiO_2 ratios for Greymouth Brunner coals plot from a near-kaolinite composition, to extremely aluminous values (Figure 7.1). Samples from the northwest area of the coalfield indicate a weakening of the hyperaluminous character in that direction (Figure 7.2). Coals from near the Spring Creek Road bridge (B9) and from Birchfield's Opencast (B1-B8) plot along the kaolinite trend in Figure 7.1, except for roof and floor samples. Approximately 1 km further northwest, coal from the New Braehead Mine contains quartz in roof and floor zones, but retains a weakly hyperaluminous character mid-seam. A Brunner seam encountered in drillhole 644 near Runanga contains abundant kaolinite, but some quartz is present and no boehmite could be detected.

To the northeast of the coalfield, two "grab" samples of Brunner coal contained mineral matter in which quartz was abundant and boehmite absent. These samples, which do not appear in the tables, were taken from an old bin site near Blackball Mine, and from outcrop at a locality known as "Brown's Lease" (Gage, 1952), located approximately midway between Blackball and the Brunnerton mines. These observations are consistent with a relatively silica-rich ash analysis for Blackball coal, listed by Hughson (1953).

Illite in Greymouth Brunner coal is very sparse throughout the bulk of the seam, but rises sharply near roof and floor as demonstrated by the Birchfield Opencast samples (B1-B8, Table 4.3). Floor samples contain a highly micaceous illite which is probably overestimated by the calculation procedure due to a high K_2O content. All of the illite-bearing samples analysed from the Brunnerton mines (largely loose coal sampled from old bin sites) probably represent roof or floor zones, or possibly sediment partings, in view of the high ash values.

Minor chlorite occurs in some of the Brunnerton coals, and traces of this mineral can be detected in LTA from both the rider seam, and the middle of the main seam, at Birchfield's Opencast Mine.

Calcite and dolomite are common in coal from the Brunnerton mines, but have not been identified in other Greymouth Brunner samples. These carbonates typically occur in the coal in a fine-grained, intimately distributed form, suggesting a diagenetic origin. The minerals are

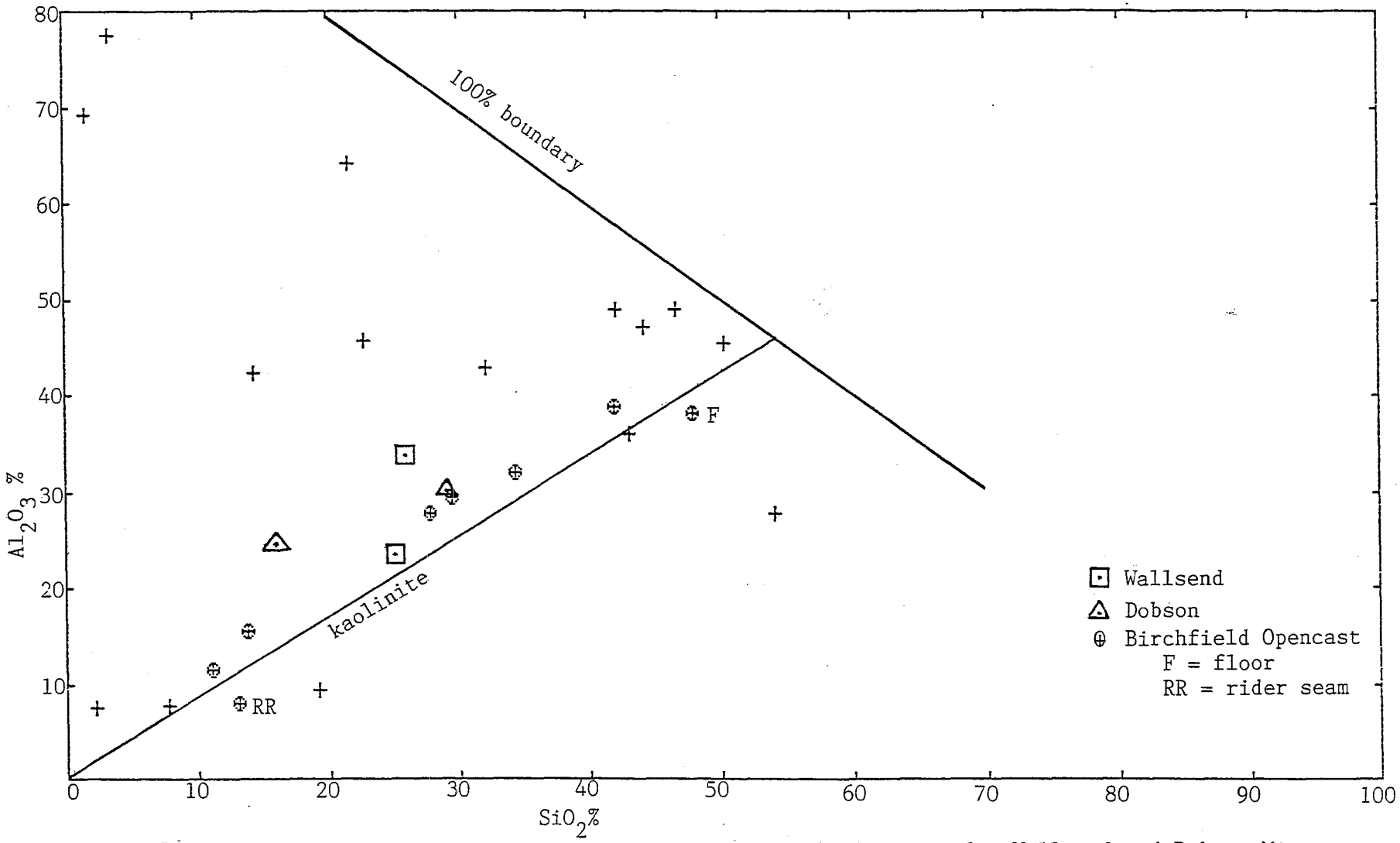


Figure 7.1 Al_2O_3 vs SiO_2 for Greymouth Brunner coal. Identified points for Wallsend and Dobson Mines plotted from data in Gage (1952).

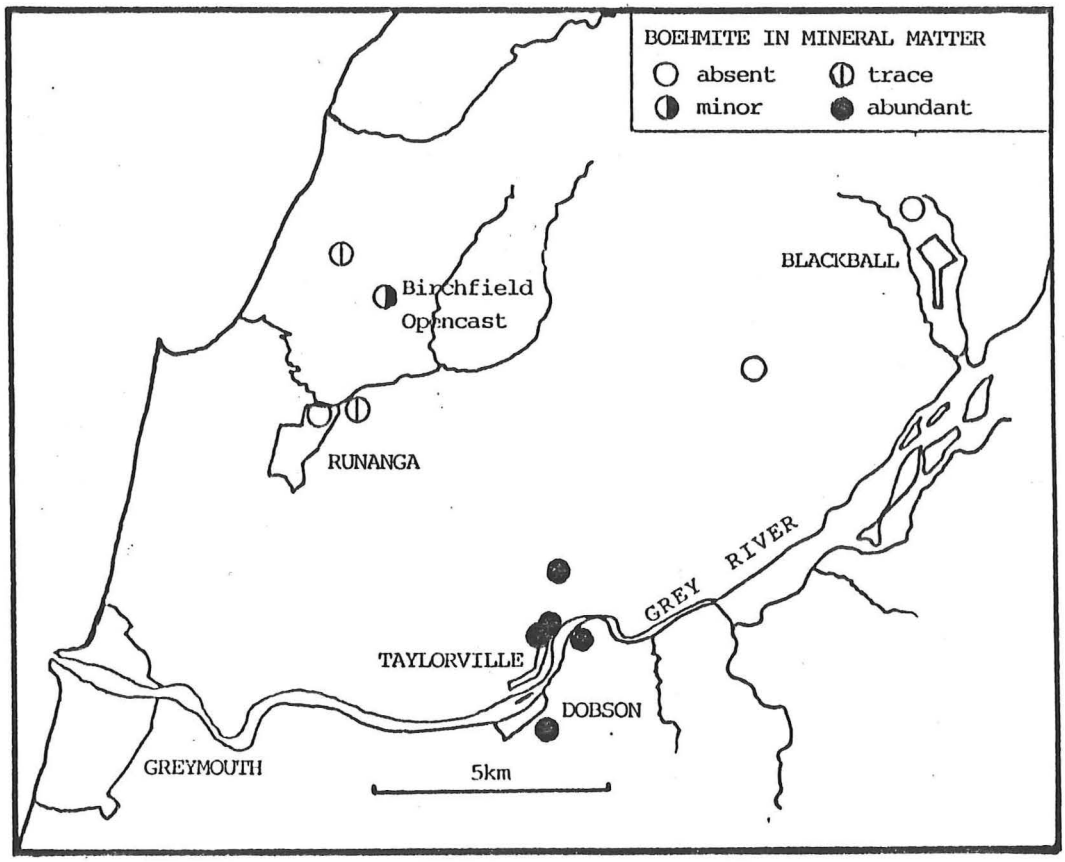
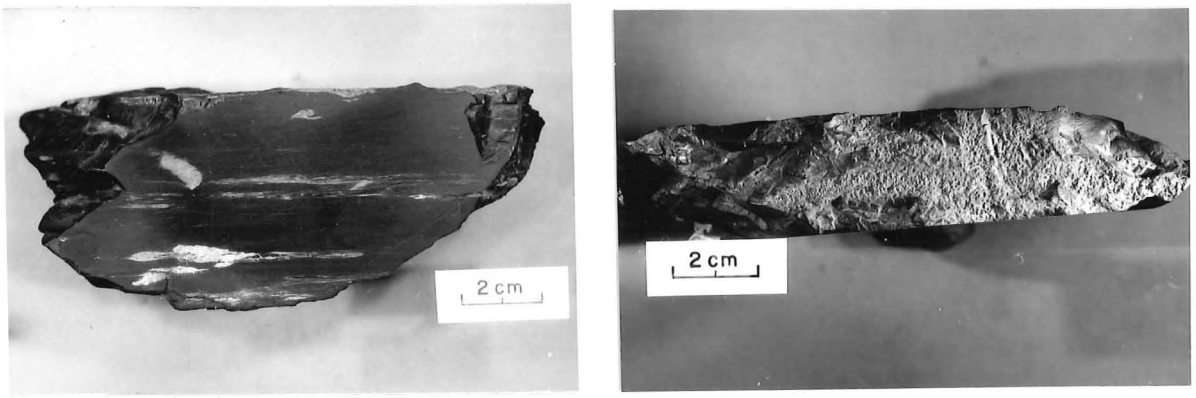


Figure 7.2 Distribution of boehmite-bearing coals, Greymouth Coalfield (Brunner Coal Measures only).



ure 7.3 Coal specimen from uppermost 0.2m of seam, New Braehead e, showing pyritised, sand-filled burrows.

t: Vertical section, showing burrows and sand laminae.
ht: Oblique-lit bedding plane surface, showing pyritised meniscus uctures.

present in some coals which show no sign of epigenetic veins; furthermore, both CaO and MgO increase sharply in the light fractions of the Tyneside Mine sample (Figure 5.4). However, epigenetic carbonates are prominent in some other samples from the same group of mines. In one such specimen from the Dobson Mine (B20), both calcite and dolomite are present, together with aragonite, which is assumed to be the cause of a high strontium value (1% Sr in ash) for this sample. Strontium-rich solutions promote the formation of aragonite, for which up to 3.87% SrO (3.27% Sr) has been recorded (Deer et al., 1962). The source of strontium in the Dobson coal may be overlying marine sandstones, which are fossiliferous.

Pyrite occurs abundantly in the northwestern coals, particularly in roof zones, whereas it is comparatively rare in Brunnerton mine samples. The upper 0.1-0.3 m of the seam in the New Braehead Mine shows pyritic replacement of sediment which infilled burrows made by marine organisms (Figure 7.3). Similar features can be seen in a thin rider seam at Birchfield's Opencast (sample B2).

Crandallite has been detected in two samples by XRD, but ash analyses suggest that this mineral is restricted to the Brunnerton mines area.

7.2.2 Interpretation

No paleoenvironmental study of the Brunner Coal Measures at Greymouth Coalfield has been documented, and petrographic investigation of the coals is limited to an early thin section study by Penseler (1933) for the James Mine, and examination of a few polished sections by J Newman and the writer. Gage (1952) provided a regional overview of the Brunner Coal Measures at Greymouth, but offered little interpretation of coal seam distribution, which is known to be "patchy". What may have been one of the most laterally persistent swamps at the time of peat accumulation was situated in the south-eastern part of the coalfield, and gave rise to the once important mining area exploited by the Brunnerton mines.

Sediments of the Brunner Coal Measures at Greymouth are highly quartzose and mineralogically mature (Gage, 1952; Smale, 1978), but it is difficult to ascertain the nature of sediments deposited in the swamps, because of alteration of inorganic matter in the peat. High ash seam bases, which contain abundant illite and kaolinite, are assumed to represent muddy deposits which accumulated in low-lying areas prior to the development of thick peat. Apart from these illite-rich zones, mineral matter in coal from Birchfield's Opencast and the Brunnerton mines is dominated by an assemblage of kaolinite, boehmite, dawsonite, crandallite, Ca/Mg carbonates, and pyrite.

(a) Boehmite and kaolinite. The abundance of boehmite in coal from the Brunnerton mines can be assigned to one or more of the following origins:

(i) In situ alteration of aluminosilicate minerals.

(ii) Influx of aluminium from outside sources, either as a detrital hydroxide, or in solution, from soil horizons surrounding the swamp.

Simple desilicification of detrital minerals, presumably illite and kaolinite, is the simplest explanation to account for the observed mineralogy in the coals. The occurrence of some very low ash samples containing relatively abundant boehmite and only traces of kaolinite strongly suggests that kaolinite has decomposed. The persistently high water table envisaged for Brunner swamps in general, on the basis of extremely sparse inertinite (Newman, 1985a), might appear unfavourable to leaching, which requires good drainage (Keller 1956; Moore 1968). However, evidence discussed in this chapter indicates that some Brunner swamps were both wet and well drained, due to continual flushing of water through the peat.

An absence of transported macerals, particularly inertodetrinite, from the coals suggests that any aluminium hydroxide brought into the swamp from an external source was very fine grained, and possibly colloidal in character. Large-scale derivation of such material from outside the swamp seems unlikely in view of the highly quartzose lithology of Brunner Coal Measures sediments, which cannot be regarded as favourable to bauxite development (Valeton, 1972). Except within the coals themselves, bauxite minerals are unknown in the Brunner sequence, and

even kaolinitic claystones are restricted to certain underclays.

To discuss the mobility of aluminium in solution, or as a colloid, and the formation and stability of aluminium hydroxides in the swamp, it is necessary to review aspects of aluminium and silicon chemistry relevant to the natural systems involved. Gross control of aluminium hydroxide and silica in a purely inorganic system is demonstrated in Figure 7.4. Under neutral or acid conditions, the solubility of amorphous silica shows little change with pH, whereas aluminium hydroxide is extremely insoluble over the range pH 8.5–4.5. Below 4.5, however, aluminium solubility rises sharply in response to the stability of Al^{3+} (Garrels and Christ, 1965).

A similar diagram has been constructed by Blatt et al. (1972) to illustrate important relationships within the low aluminium solubility region near neutral pH (Figure 7.5). However, the inferred stability fields shown in this diagram cannot represent equilibrium conditions, in which amorphous silica would be absent, and the kaolinite field would extend to lower solubilities. Stability fields for aluminium hydroxide and kaolinite in simple, inorganic systems at equilibrium are shown in Figures 7.6 and 7.7, both adapted from Garrels and Christ (1965). The aluminium hydroxide shown in these diagrams is gibbsite, which is the species commonly synthesised under acid conditions in experimental systems. The origin of boehmite in West Coast coals, in preference to other hydroxide forms, is discussed in the following chapter.

In natural aluminium hydroxide/silica systems, the stability boundaries are subject to the following complications:

(i) Boundary location is influenced by dissolved inorganic species other than those of aluminium and silicon, and also by the type of aluminosilicate and hydroxide mineral in equilibrium with the solution. In a well-leached nonmarine swamp environment, dissolved species other than silicon and aluminium are unlikely to be abundant, although some K^+ will be released by degrading and decomposing illite. Of probably greater influence is the mineralogy and crystallinity of the principal mineral components; in general, the well-crystallised minerals show a much lower solubility than do microcrystalline, disordered, or amorphous forms. Figure 7.8,

adapted from the work of Lind and Hem (1975) shows how the pH-solubility curve for aluminium is displaced vertically by the presence of different solid phases.

(ii) Formation of organic complexes enhances the solubility and transport of both aluminium and silicon. Stabilisation of dissolved silica has long been suspected (e.g., Blatt et al., 1972; p250), but proof of this reaction has only recently been demonstrated (Bennet and Seigel, 1987). Similarly, a number of low molecular weight organic acids are known to enhance aluminium solubility, as demonstrated and discussed by Huang and Keller (1970, 1971, 1972a, 1972b), and Lind and Hem (1975). The latter authors show how the formation of alumino-complexes can allow dissolved aluminium to reach 10-100 times the concentration predicted by temperature/pH conditions for pure water (Figure 7.8).

(iii) Naturally occurring, high molecular weight organic compounds also form alumino-complexes, and can incorporate aluminium in colloidal particles. Lind and Hem (1975) attribute part of the apparently dissolved aluminium in naturally coloured waters to such colloids. On the basis of experimental work, these authors believe that organic compounds facilitate the growth of well-crystallised aluminosilicates, if sufficient dissolved silica is present, by inhibiting polymerisation of aluminium hydroxide.

At the time of writing, more than a decade after the work of Lind and Hem (1975), little more is known about the stability of simple aluminosilicates and bauxite minerals in natural systems. The outstanding problems are summed up by Bilinski et al., (1986):

"...the systems are both complicated and time-dependent and therefore experimental studies are difficult to perform and interpret. A characteristic feature of most natural systems is the presence of a multiplicity of different organic species all of which may form complexes with aluminium and thus cause a considerable enhancement of mineral solubilities."

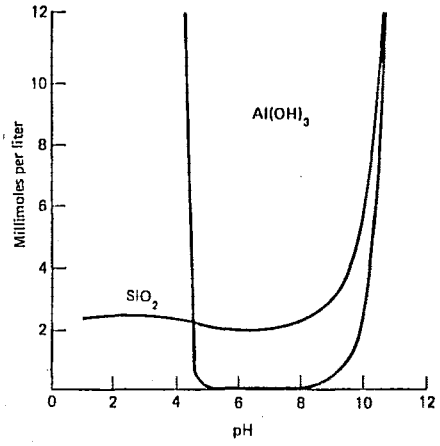


Figure 7.4 Solubility of amorphous silica and aluminium hydroxide as a function of pH. From Mason and Moore (1982).

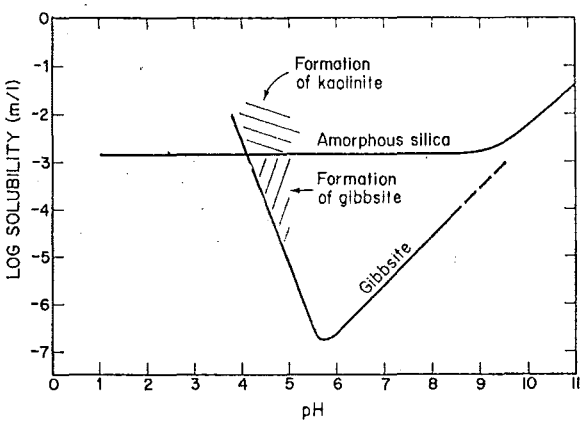


Figure 7.5 Solubility of amorphous silica and gibbsite as a function of pH. Adapted from Blatt et al. (1972).

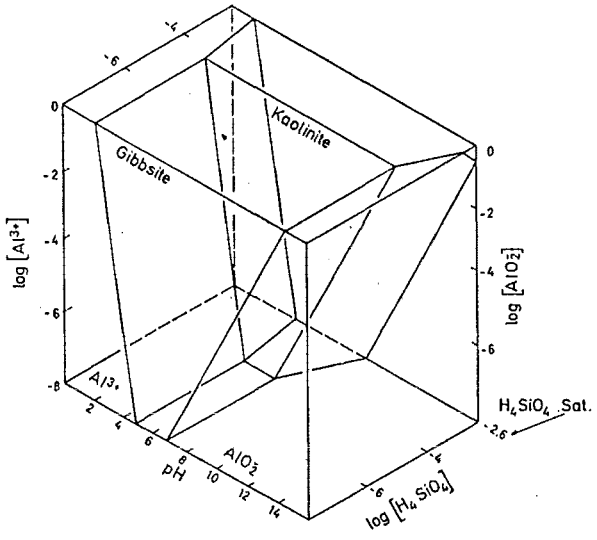


Figure 7.6 Kaolinite-gibbsite stability relationships, as a function of pH, dissolved aluminium, and dissolved silica. From Garrels & Christ, 1965).

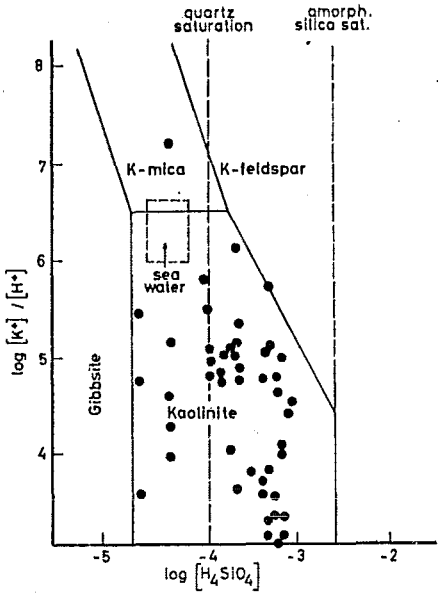


Figure 7.7 K-aluminosilicate stability fields, from Garrels and Christ (1965). This diagram is used to clarify the kaolinite-gibbsite join on a dissolved silica axis, and the saturation limits of quartz and amorphous silica.

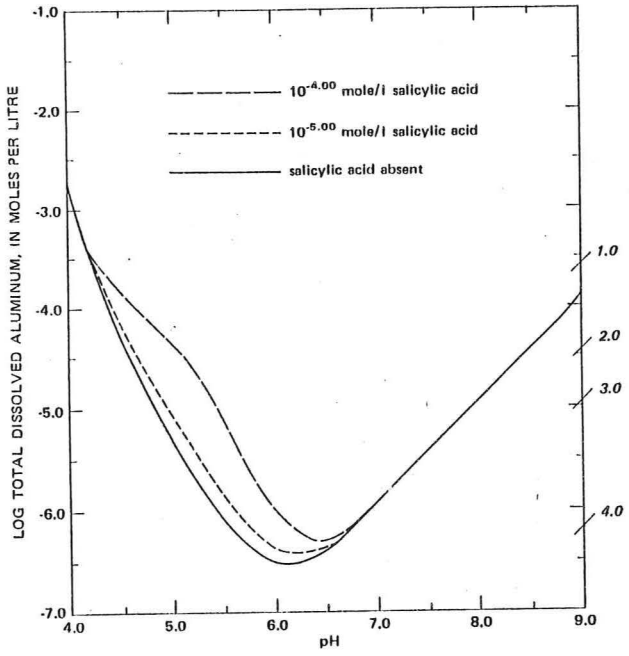


Figure 7.8 Solubility of synthetic halloysite in presence of $10^{-3.48}$ mole silicic acid (20mg/1 SiO_2), represented by solid curve.

Numbers at right margin show intercepts for similar curves produced by other compositions:
1. Fresh aluminium hydroxide precipitate (high pH), microcrystalline gibbsite (low pH), no silica.
2. Synthetic halloysite, 60mg/1 SiO_2.
3. Crystalline bayerite (high pH), gibbsite (low pH), no silica.
4. Crystalline kaolinite, 20mg/1 SiO_2.

Dashed curves show the effect of an organic acid. From Lind & Hem (1975, Figure 5).

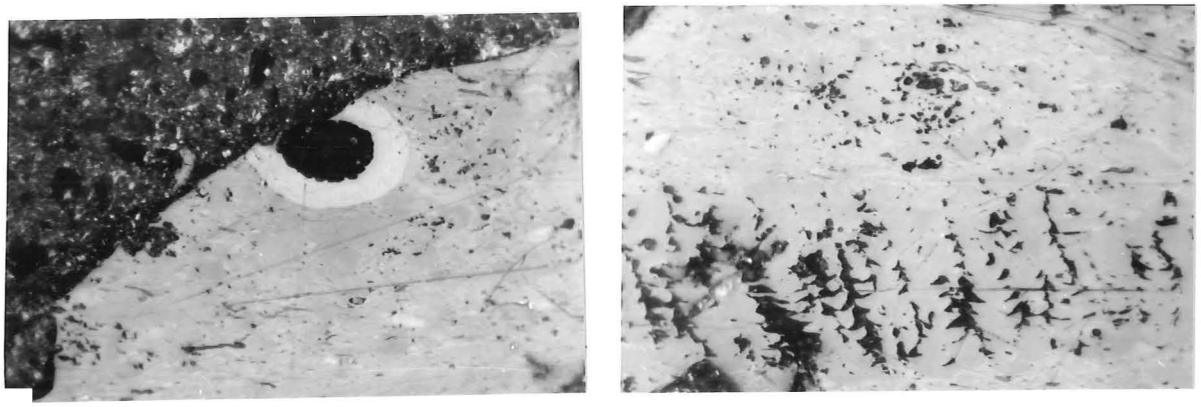


Figure 7.9 Kaolinite and boehmite from the Brunner Mine portal.

Left: Fungal spore infilled by authigenic clay. Dark material at upper left is mounting medium.
Right: Partly collapsed cell structure infilled by authigenic clay, which is also finely distributed throughout the coal.

The featureless, highly degraded and vitrinite dominated maceral assemblage is typical of coals from the Brunnerton Mines.

Despite the uncertainties arising from the complex chemistry of natural systems, it is possible to draw some broad conclusions concerning the geochemistry of the "Brunnerton swamp". The hyperaluminous characteristic of many of these coals is compelling evidence that free silica has been lost and some kaolinite decomposed. It appears that a balance of drainage and acidity was maintained so as to allow the swamp to become a net accumulator of aluminium, and undergo a net loss of silica. Widespread distribution of boehmite-kaolinite mineralisation, both laterally and vertically within the full seam thickness indicates that stable, oligotrophic, well drained conditions persisted throughout peat accumulation.

Although aluminium may have been derived in solution, or as a colloid, from groundwater draining surrounding, organic-rich areas, this is entirely hypothetical in the absence of independent evidence of such source areas. If aluminium influx did take place, hydroxide precipitation probably occurred in response to a pH gradient, rather than simple concentration by evaporation/transpiration, which would also concentrate silica. Retention of aluminium in the peat would have been favoured by a relatively high pH, which is consistent with the extreme tissue degradation seen in polished sections of coal from the Brunnerton mines (Figure 7.9). Stabilisation of aluminium hydroxides may have been achieved by diffusion or gradual flow of solutions from an acidic surface zone into the underlying peat, where pH is known to rise with depth (Waksman and Stevens, 1929; Teichmüller and Teichmüller, 1982).

Relatively good drainage of the Brunnerton peat is also suggested by the existence of high-alumina fireclays beneath the seam in some parts of the Brunnerton mines (Gage, 1952); good preservation of leaf-fossils within this material suggests that it was not highly weathered as a fossil soil, but probably underwent alteration as a result of downward drainage by acid, silica-undersaturated solutions from the overlying peat (e.g., Staub & Cohen, 1978).

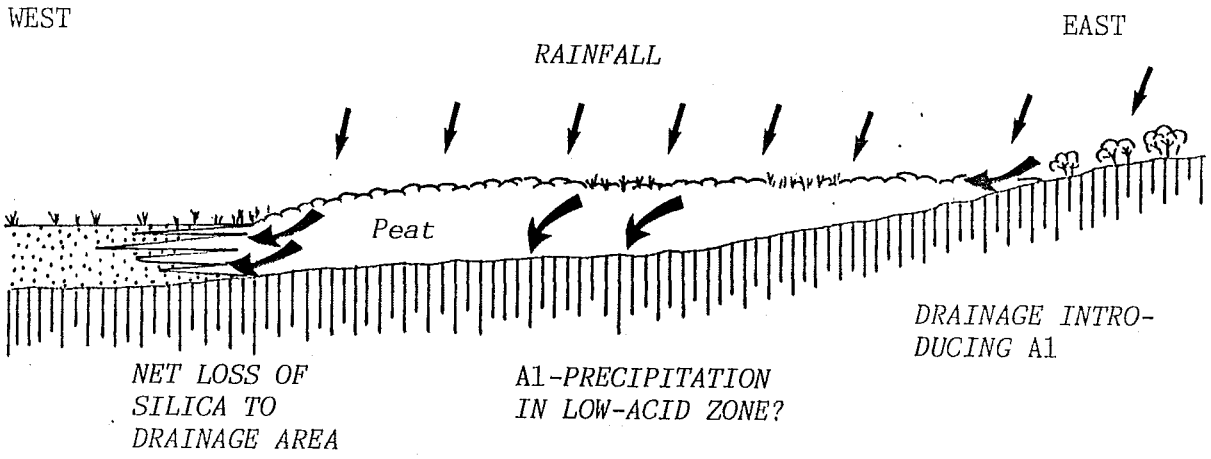


Figure 7.10 Diagrammatic representation of suggested depositional setting for Brunnerton coals (Brunner Coal Measures, Greymouth Coalfield). The Brunner swamp rests on a local basement of underlying coal measures at the eastern margin of the basin, and passes westward into a fluvial drainage area. Al = aluminium.

Figure 7.10 shows a suggested reconstruction of the Brunnerton swamp profile. Immediately west of the area is a trough axis (Gage, 1952) where Brunner coals are thin and severely split, possibly representing a fluvial drainage zone, whereas to the east, both the coal and coal measures thin abruptly on the margin of a stable block.

Pollen dating of the Brunner sequence at Birchfield's Opencast indicates that the thick seam at this locality is at least partly of Paleocene age, i.e., "Brunner P" of Nathan et al., (1986) shown in Figure 1.9. The seam is overlain by marine sandstone containing a thin rider seam, for which middle Eocene dates were obtained (Newman, 1985a). Newman describes the Birchfield Opencast succession as conformable, and concludes that the main seam must represent a time span of some 8 M years. In contrast, Brunner seams from the far north-west of the coalfield and from Blackball have been dated as middle Eocene, and are overlain by rocks of similar age (Nathan et al., 1986).

Although palynological age determinations for coal from the Brunnerton mines have not been completed, provisional results indicate the presence of a Paleocene flora similar to that recorded from the Birchfield Opencast (S Nathan, pers. comm). This evidence suggests that extreme swamp longevity may be a major factor controlling desilicifica-

tion and aluminium concentration of these coals. If input of sediment to the swamps was minimal, and oligotrophic conditions persisted, the effects of only slight or periodic leaching would be cumulative.

Mineral genesis in the Birchfield's Opencast peat appears to have been restricted chiefly to kaolinite formation (Figure 7.1). As the main seam at this locality appears to be of similar age to the Brunnerton coal, the mineralogical differences between these two coals are assumed to arise from paleoenvironmental differences. A general absence of peraluminous mineral matter in the Birchfield coal suggests an absence of intense or prolonged leaching. If both swamps experienced similar climatic conditions, the mineral matter differences must be attributed to either superior drainage of the Brunnerton swamp, or lack of transported aluminium at the Birchfield site. Both factors may have been significant.

The chlorite content of the marine-influenced Birchfield's rider seam may represent detrital material, but it seems unlikely that detrital chlorite could survive in the Brunnerton swamps. An authigenic origin, related to the hyperaluminous character of the coal is proposed and discussed in the following chapter.

(b) Sulphides and carbonates. At the northwestern Brunner localities, marine sandstone rests directly on the coal seams, resulting in a generally higher sulphur content for these coals than for the Brunnerton Mines. Sulphur enrichment is accompanied by an increase in pyrite as a proportion of total mineral matter (Tables 4.3, 4.5). These effects are extreme at the New Braehead Mine and nearby workings (e.g., Jubilee, James, and Bellevue Mines) where the uppermost part of the seam may have accumulated under intermittently marine conditions, as suggested by pyritised sand which infills burrows and forms thin laminae (Figure 7.3). Penseler (1933) attributed the degraded texture and perhydrous character of coal from the James Mine to accumulation under brackish conditions. Similarly, the rider seam at Birchfield's Opencast exhibits abundant burrows and sandy laminae and is known to contain marine dinoflagellates (Raine, 1982). The presence of the rider seam at the Birchfield Mine, however, probably limited postdepositional sulphur enrichment of the main seam, which contains about 1% total sulphur ove-

rall, whereas some of the mines near the New Braehead workings produced run-of-mine coal containing more than 7% sulphur. Data from Budge and MacKnight (1976) indicate that more than half the total sulphur in these high sulphur coals is pyritic.

Much of the pyrite in the western coals is very fine grained, as shown by the increasing proportion of pyrite in the successive float fractions of the Brunner sample from drillhole 644 (Table 4.3). This fine pyrite may indicate input of brackish water during peat accumulation (King and Renton, 1979).

It is not clear why carbonate minerals are absent from the western Brunner coals. The conventional view of "brackish influenced" coals suggests that concretionary dolomite should be present (e.g., Teichmüller, 1982; Mackowsky, 1982). Although dolomite deposition may have been suppressed by high sulphate levels (Curtis and Coleman, 1986), some calcite would be expected.

Carbonates in the Brunnerton coals are predominantly fine-grained and intimately dispersed, although some epigenetic material is present. The fine-grained carbonate appears to represent a mineral occurrence not previously reported from coal. The uniformity of carbonate distribution reflects an organic association, as shown by the restriction of most CaO-in-coal values to a range 0.2-0.3%, except for high ash coals or where epigenetic veins are present. This character is also demonstrated by CaO and MgO values for the density fractions of sample B14, which shows a well-defined organic association for which CaO-in-coal is 0.29 ±0.01 (Figure 5.4). A diagenetic origin during deep burial is discussed in the following chapter.

The epigenetic carbonates probably result from fracture formation during and after regional uplift, and may represent simple remobilisation of the fine-grained carbonate, or derivation from some external source. The strontium-rich aragonite (B20) may have developed from solutions transporting biogenic carbonate from the overlying marine Island Sandstone.

(c) Minor constituents. The Greymouth Brunner coals contain remarkably low TiO_2/Al_2O_3 ratios, except in the case of the illite-rich samples for which the ratio rises sharply to equal some of the highest values noted for Paparoa coals. This characteristic is well demonstrated by the Birchfield Opencast samples (Figure 7.11). If calculated percentages for rutile and illite are graphed, a well-defined positive correlation is observed (Figure 7.12); a single "fallout" point represents an anomalous, P_2O_5-rich sample (B16). This correlation is unique to the Greymouth Brunner coals.

The higher TiO_2 values at the seam floors may represent a titanium-rich micaceous sediment derived from a landscape rich in residual minerals during the onset of peat accumulation; Smale (1978) noted a relative abundance of rutile, anatase and brookite in Greymouth Brunner

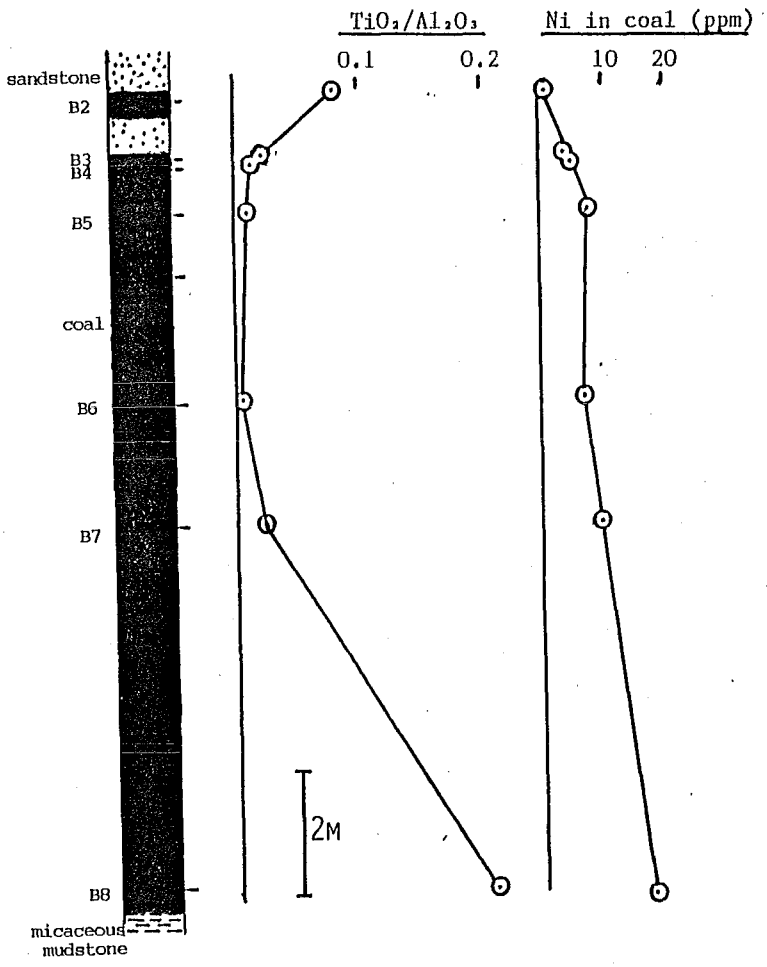


Figure 7.11 Column showing sample positions within the Brunner seam at Birchfields Opencast, Greymouth Coalfield, and vertical variation in TiO_2/Al_2O_3 and nickel.

Coal Measure lithologies in comparison to rocks of the Paparoa Coal Measures. However, chemical origins must also be considered, e.g., titanium accumulation in the peat during an early minerotrophic phase, and/or subsequent precipitation from descending swamp water in a low-acidity zone near the base of the peat.

Nickel values are low throughout the body of the seams and rise sharply at the floors, although on a nickel-in-coal basis there is little change thoughout the seams (Figure 7.11; Table A2.2, Appendix 2). It is notable that the lowest nickel concentrations occur in the "marine-influenced" coals at the western mines, i.e., seam roofs, the middle and upper New Braehead samples, and Birchfield's rider seam. It therefore appears unlikely that nickel in Greymouth Brunner coals was derived from marine water, even though modern seawater is known to contain substantially more nickel than freshwater (Mason and Moore, 1982). The evidence also suggests that the peat was highly trace metal-deficient at the time of burial, and failed to adsorb nickel from groundwater after burial. There is no correlation of nickel values with pyritic iron.

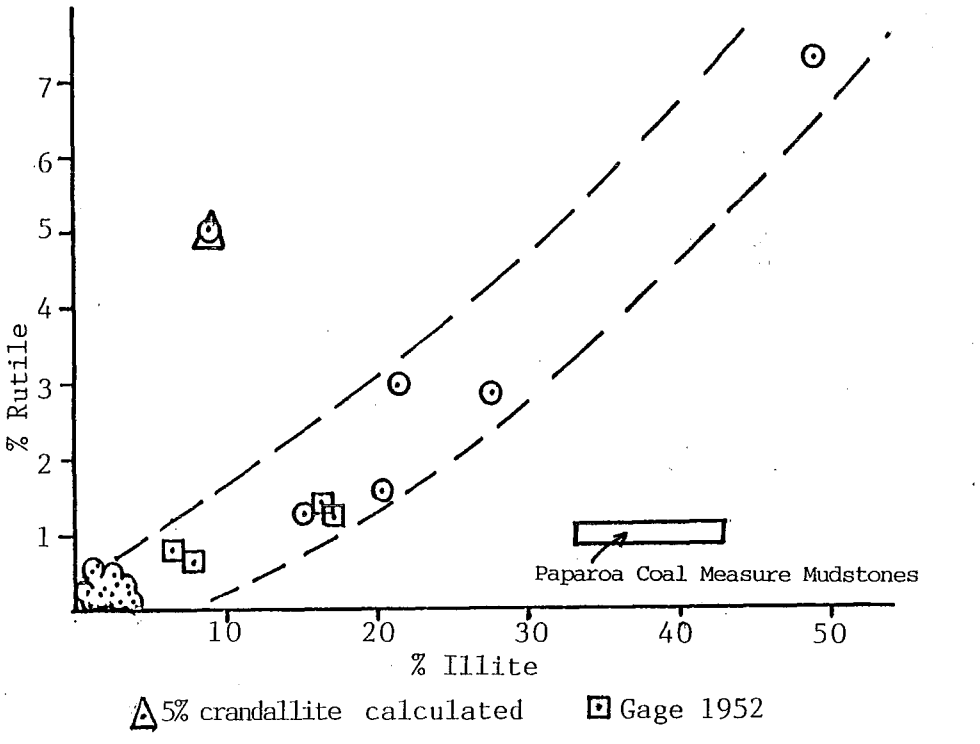


Figure 7.12 Calculated rutile vs calculated illite for Brunner coals, Greymouth Coalfield.

7.3 PIKE RIVER COALFIELD

7.3.1 Minerals in Pike River Brunner Coals

A single, thick Brunner seam occurs throughout Pike River Coalfield, where it rests on a very thin sequence of quartzose Brunner Coal Measures overlying Paparoa Coal Measures (Figures 1.7, 4.5). In most subsurface locations the seam is overlain by a rider seam, which is separated from the main seam by silts interpreted as lagoonal deposits (Newman, 1985a). Marine sandstone (Island Sandstone) overlies the rider seam, or the main seam where the rider is absent. Where marine sandstone roofs exist, there is evidence of burrowing, and in some cases of erosion of surface peat prior to sandstone deposition.

Outcrop samples analysed prior to drilling of the Coalfield showed a strong domination by quartz and pyrite (Table 4.3), but one intersection was found to contain abundant dolomite and calcite. Subsequently, analysis of drillhole samples showed that these carbonate minerals dominate the mineral assemblage; substantial loss of carbonate by weathering is indicated. This effect is further demonstrated by the presence of voids and oxide pseudomorphs after pyrite, seen in polished section. Surprisingly, gypsum was sparse in the outcrop coals, presumably because of the extremely high rainfall at the coalfield, in combination with very good drainage from the cliffside exposures.

High sulphur samples from the rider seam, or from the top of the main seam, are rich in pyrite which is typically framboidal, although a range of sulphide morphology is present (see Illustrations, Chapter 3); framboidal pyrite is rare in other West Coast coals. Concentration of pyrite along sediment microlaminae suggests some replacement of detrital mineral matter.

7.3.2 Interpretation

The only paleoenvironmental work done on the Pike River Brunner coals are studies by Newman and Newman (1982), based on outcrop coals, and by Newman (1985a), who incorporated additional samples from 6 drillholes. Newman envisages peat accumulation in a back-barrier marginal

marine environment, where water tables gradually rose, producing a gradual change in coal properties throughout the seam thickness. Sulphur enrichment is considered to reflect some influx of brackish water to the peat, and post-depositional enrichment, depending on proximity to the marine environment and character of roof and floor sediments. When Newman (1985a) attempted to reconstruct a depositional model for the Brunner horizon, evidence from petrography and stratigraphic sections failed to agree with the distribution of ash values for the seam. However, the true pattern of clastic sedimentation was obtained by recalculating ash values to eliminate authigenic carbonates, using a method supplied by the writer (see Chapter 8).

(a) Quartz and silicates Detrital mineral matter is clearly dominated by quartz, especially in the outcrop area which Newman (1985a) considered to represent the margin of a high ash area. A graph of Al_2O_3/SiO_2 (Figure 7.13) shows that most compositions fall far from the kaolinite line, confirming Newman's petrographic observation of sparse, isolated quartz grains in low ash coal. Newman (pers. comm.) believes that sporadic grains and laminae of quartz sand in southern locations can be attributed to washover effects at the barrier bar during peat accumulation. However, such an origin, which implies significant transport energy and can be seen to have caused seam splitting and high ash zones in the south, cannot be applied generally. If a correction is made for the carbonate and pyrite content, the seam in the central and northern parts of the coalfield must be regarded as extremely low ash (commonly <1%). Potential origins for detrital minerals in more northern locations are either deposition of grains from rafted vegetation, or possibly windblown material transported from the barrier bar. Eolian transport alone is unlikely to have produced the widespread distribution pattern observed, whereby quartz in the coal is abundant (relative to kaolinite) throughout the coalfield and vertically throughout the seam. "Chuckie stones" are absent, which is consistent with a source area of very low relief, and an absence of major streams near the swamps.

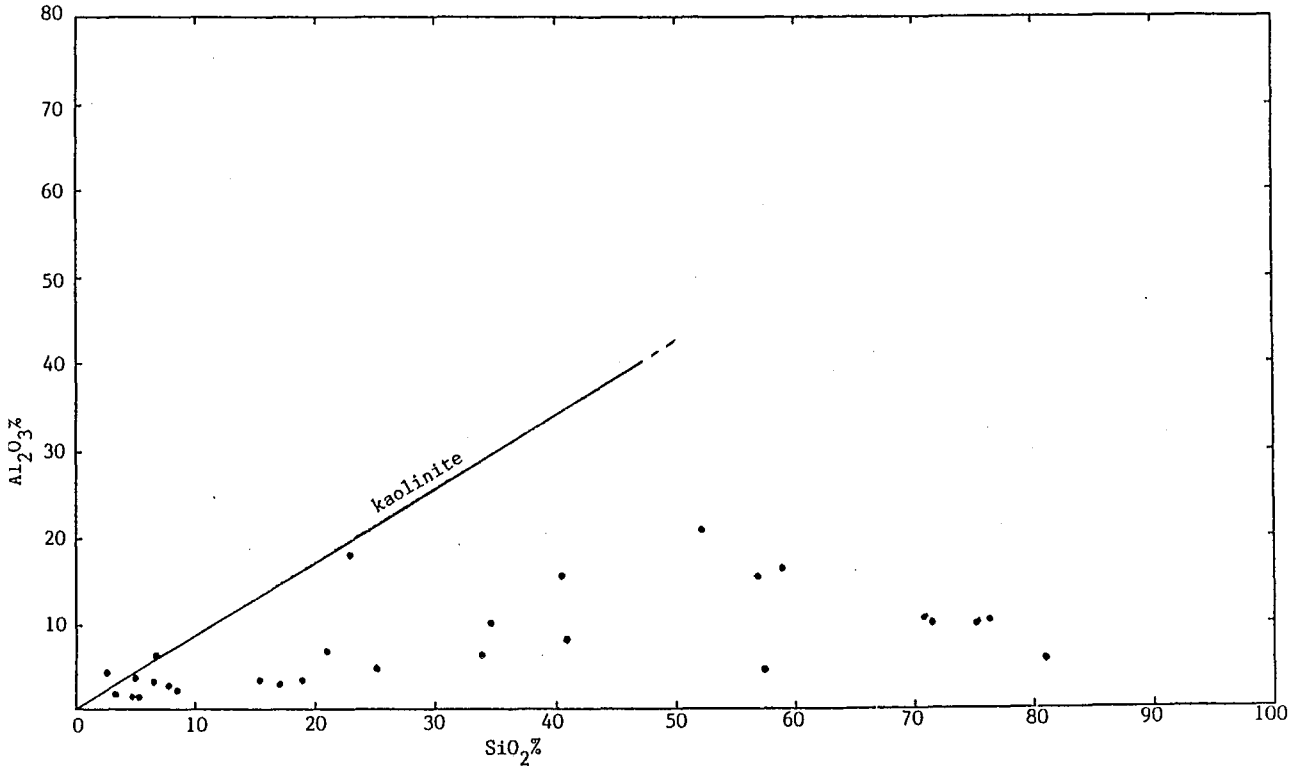


Figure 7.13 Al_2O_3 vs SiO_2 for Pike River Brunner coals.

Sparse samples show a moderately hyperaluminous composition (Figure 7.13), and boehmite reports in the calculated minerals (Table 4.3), particularly for sample 33/006. Boehmite was not observed in whole LTA for this coal, although acid treatment was not carried out to remove the carbonate component prior to XRD. The light, ultra-low ash fractions of sample 30/121 also show a hyperaluminous composition, but were not analysed by XRD. These data suggest that some leaching of mineral matter in the peat took place, but to a very limited extent.

Survival of relatively abundant quartz, particularly of rafted origin, suggests a persistently high water table for the swamps. This view is entirely consistent with Newman's (1985a) conclusion that the Pike River Brunner swamps were poorly drained, relatively alkaline (i.e., only weakly acidic), and poorly oxygenated. Earlier, Newman and Newman (1982) had related this paleoenvironmental interpretation to the anomalous characteristic of the vitrinite, which shows a mean maximum reflectance (R_{mo}) some 0.3% lower than "normal" vitrinites of the Paparoa Coal Measures, less than 200 m beneath the Brunner seam.

(b) Carbonate minerals X-ray diffraction shows that dolomite is the major carbonate present, commonly accompanied by lesser amounts of calcite. A good correlation between MgO and CaO, especially for the drillhole samples, confirms this observation (Figure 5.18). In polished section, the carbonate minerals are seen to be located in fracture zones where the coal shows widespread evidence of fluidisation and flowage. The thorough "healing" shown by this fractured material, together with textures indicating some compaction after veinlet emplacement, suggest that the carbonate was introduced or remobilised comparatively early in the coalification history of the seam.

Carbonate deposition in the Pike River Brunner coal can be attributed to any one of the following causes:

(i) Redistribution of existing, syndepositional carbonate within the Brunner seam.

(ii) Postburial carbonation of Mg and Ca absorped by the peat after marine inundation of the swamps.

(iii) Downward percolation of solutions from the overlying, calcareous Island Sandstone.

Of these possibilities, (i) or a combination of i) and (ii) seems the most probable explanation. Some carbonate can be seen preferentially located within stem centres (Figure 3.6 a), or within bands occupied by single telocollinite macerals, suggesting very early emplacement. Syngenetic dolomite is considered typical of coals which were influenced by marine water during peat accumulation (Mackowsky, 1982).

However, the massive, dolomitic "coal balls" described by Mackowsky are absent, and the paleoenvironmental interpretation of Newman (1985a) for most of the seam does not favour the *strongly* brackish swamp environment which is believed to give rise to authigenic, concretionary dolomite and calcite (e.g., Techmüller and Teichmüller, 1982). In view of these constraints, option (ii) is preferred.

It is notable that analyses for the unweathered drillhole samples show calcium/sulphur ratios similar that of modern seawater (Mason and Moore, 1982), which is considered to have undergone little change in composition since Paleozoic time (Garrels and MacKenzie, 1971). This

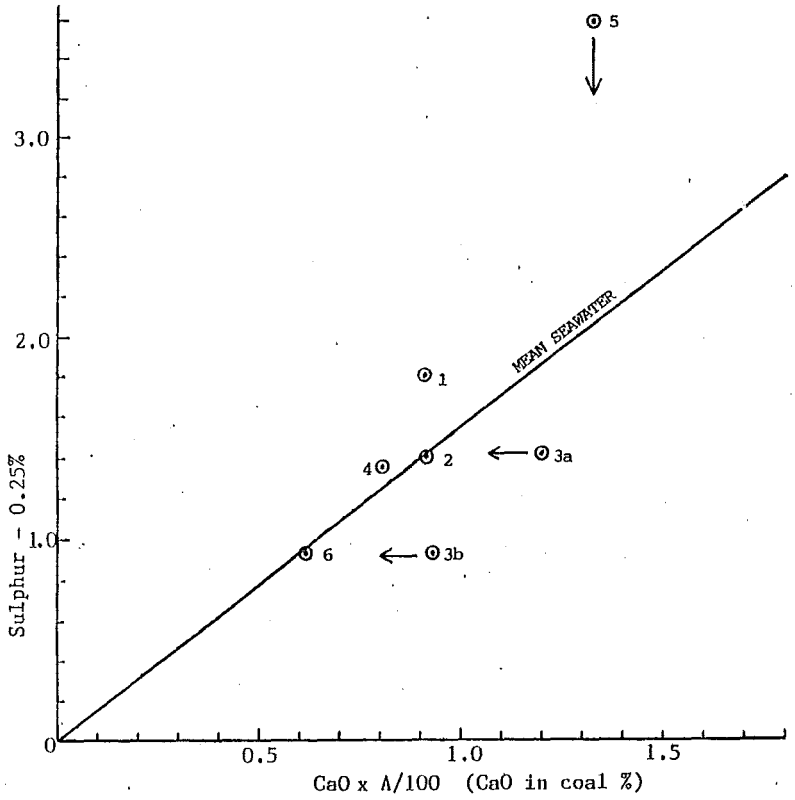


Figure 7.14 Total sulphur/CaO relationships for whole coal, computed for full thickness of the Brunner seam at Pike River Coalfield. Numbered points show drillhole numbers (Figure 4.5). Points 3a, 3b represent inferred seam repetition by faulting.

similarity becomes even closer if a small (0.25%) sulphur correction is subtracted to allow for "vegetal" sulphur content displayed by fresh-water coals lacking sulphur enrichment (Figure 7.14). The fallout points can be attributed to (i) an excess of late-stage sulphur, derived by lateral migration via a permeable horizon, and (ii) excess calcium caused by epigenetic veins associated with faulting. Ply analyses tend to show an increase in Ca/S ratio downwards through the seam, possibly resulting from a difference in rates of diffusion and reaction for the two components. However, the relationship shown in Figure 7.14 is obtained by plotting values for full-seam intersections, suggesting that for a unit volume of marine water which equilibrates with the peat, complete adsorption of sulphur and calcium has been achieved.

No similar relationship can be observed for Mg/S ratios, indicating incomplete magnesium adsorption. Curtis and Coleman (1986), discussing marine incursions over coal measures, point out that precipitation of magnesium carbonates is initially inhibited by high sulphate concentrations. Much of the magnesium, therefore, may have been lost in expelled pore water.

The data points used to support this hypothesis are few, but further testing of the observed relationship must wait until further drilling of the deposit is carried out. Other Brunner coals, even where a marine roof is present, contain too little calcium to conform to the relationship demonstrated above. The reason for the high calcium and magnesium content of the Pike River Brunner seam is not immediately apparent. However, it is notable that the Pike River seam may represent an extremely high water table, low acidity peat, in which exchange site occupation by Al^{3+} can be expected to be minimal.

(c) Minor constituents. The concentrations of TiO_2, Na_2O, and Ni in whole coal tend to be low and uniform, even if allowance is made for dilution by the major authigenic minerals. However, TiO_2/Al_2O_3 ratios do not exhibit the extremely low values observed at Greymouth. Unfortunately the Ni data are too few, and the ply intervals too large, to identify possible nickel enrichment of floor coals as recognised for the Greymouth Brunner coal, although very low nickel values correspond to top plies in both deposits.

7.4 BULLER COALFIELD

7.4.1 Minerals in Buller Coals

At Buller Coalfield (Figure 4.6), only Brunner coal is present. Most of the mining areas shown are largely worked out by underground operations, but many are now being considered for further coal recovery by opencast mining. Recently, unexploited areas of recoverable coal have been located by drilling in the Upper Waimangaroa valley.

In the Millerton-Stockton mines area, there are substantial deposits of coal which may be unique in the world with respect to their low ash value, e.g., of the 16 M.t. Webb/Baynes Block, drillhole ply composites indicate 2 M.t. <1% ash, and more than half of this averages <0.5% ash (Marshall, 1983). Low ash blocks are found elsewhere in the coalfield, but not of the same extent and thickness.

A thick, low ash seam is worked in opencast mines at the Webb/Baynes locality, producing a high-quality coking coal which is exported for special metallurgical use and activated carbon manufacture. A recent study demonstrated the suitability of this coal for aluminium smelter anode production (Marshall, 1983), although to date, projected production costs have shown such an industry to be uneconomic unless the value of the product rises substantially.

The Buller samples examined in this work do not provide a complete coverage of this extensive coalfield. Direct mineral matter analyses by LTA-XRD procedure have been carried out for only the samples listed in Table 4.3, i.e., some field samples, run-of-mine samples, and selected plies and composites from the Webb/Baynes Block drillcore.

The analyses indicate a highly variable mineral assemblage, even within the restricted area of the Webb/Baynes Block. Some low ash coals are distinctly boehmite-bearing, as are both floats and sinks from the Baynes barren belt, a high ash zone near the Stockton Opencast. Pyrite occasionally dominates, particularly in high-sulphur areas and near seam roofs. Illite is common, and is abundant in high-ash zones such as the barren belts, and in rare horizons within the low ash zones. Several of the Buller spot samples and composites contain a higher chlorite content than observed in any other West Coast coal. However, it appears that chlorite has a restricted distribution, and may not comprise a significant component in whole-seam or run-of-mine mineral matter. Gaigher (1981) reported chlorite as a major clay mineral in an ultra-low ash Stockton coal, but the interval represented by the sample is unknown.

The presence of illite-rich horizons in otherwise low-ash Webb-Baynes coals is assumed to be one cause of anomalous downhole logging reponses reported from these coals, wherein the natural gamma intensity has indicated mudstone in intervals known from core and cuttings to be coal (Mr R Parsonson, BPB Instruments Ltd., pers. comm.). A combination of high potassium-in-coal, and a low ash, low mass absorption matrix can be expected to greatly enhance the ^{40}K natural gamma flux.

As a result of an extended period of shallow burial after uplift, much of the Buller coal shows some degree of weathering, particularly near fault zones or beneath jointed cover. In these circumstances, oxidation of pyrite, redeposition of iron as limonite, and alteration of calcite to gypsum have been noted. Samples from drillhole 1241 contain up to 11% K_2O in ash (Table A2.4, Appendix 2), which is too much potassium to be accommodated by the range of silicate minerals normally present in the coals, and indicates that potassium sulphate minerals have accumulated in the seam in response to weathering of the overlying rocks. Such "high gamma" holes have produced anomalous coal quality logs. The potassium mineralisation is assumed to be jarosite, $KFe_3(SO_4)_2(OH)_6$, which is visible on freshly exposed joints in sandstones, and possibly also alunite, $KAl_3(SO_4)_2(OH)_6$. Formation of these minerals can be attributed to recent weathering of pyrite to produce acid, iron-bearing solutions which attack both illite and residual feldspar in coarse sandstones overlying the coal seam. This mineralisation may also occur in some old (>20 yrs) drillholes which were relocated and logged by downhole sensing, and proved to be "high gamma", whereas fresh holes drilled nearby gave a normal response.

7.4.2 Interpretation

(a) Regional paleoenvironmental setting. The only detailed paleoenvironmental works documented for the coalfield to date are a study of the Webb-Baynes block (Newman, 1985a) and a report covering the Upper Waimangaroa Valley area (Newman, 1986). General geological mapping, summarised by Nathan et al. (1986), indicates that a marine gulf was located to the south of the coalfield during Eocene time. The headward region of this gulf is interpreted by Newman (1986) as a low-lying area containing an axial fluvial system bordered by peat swamps (Figure 7.15). Lateral migration of the fluvial system is considered to have allowed intermittent invasion of brackish water in abandoned overbank areas, and seam splitting by fluvial sediment in the proximity of channels. A large variation of swamp types is recognised, ranging from high-moor to low-moor, and brackish (Figure 7.16), on the basis of seam character and coal type.

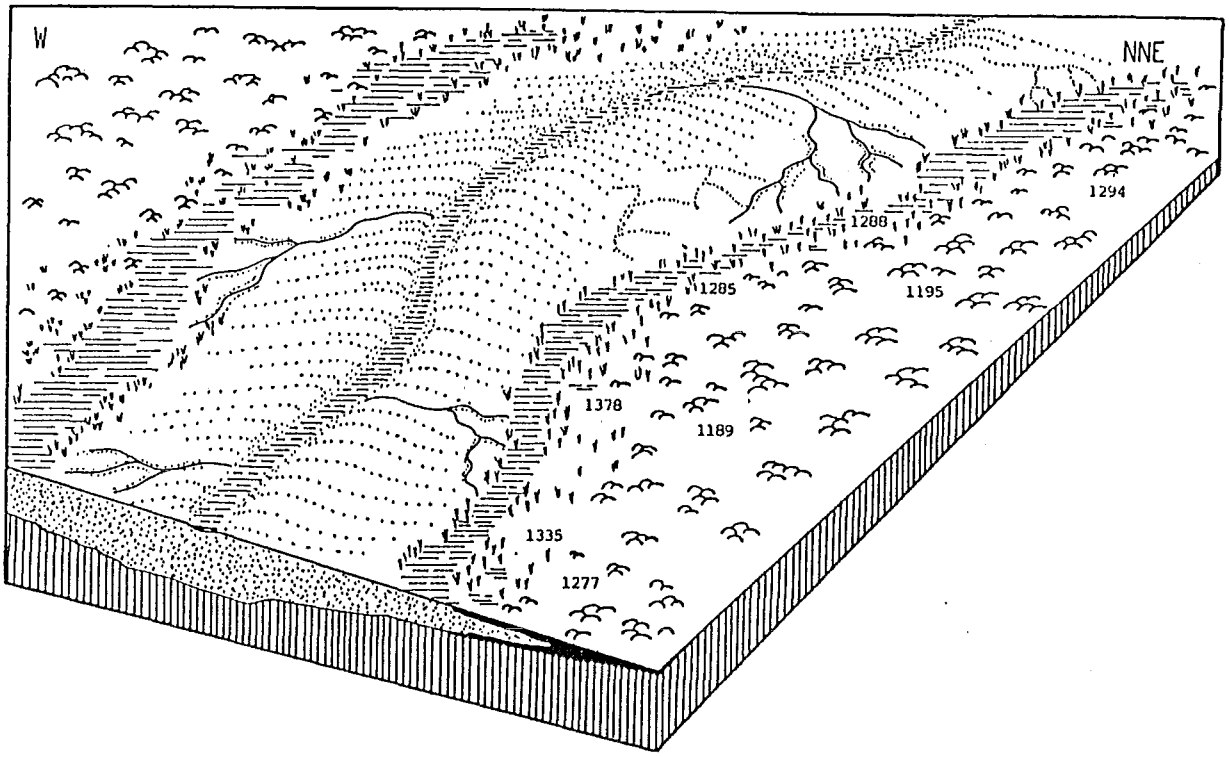


Figure 7.15 Suggested paleogeography for Brunner Coal Measures in the Upper Waimangaroa Sector of Buller Coalfield. Drillhole numbers delineate the position of the Sector. From Newman, (1986).

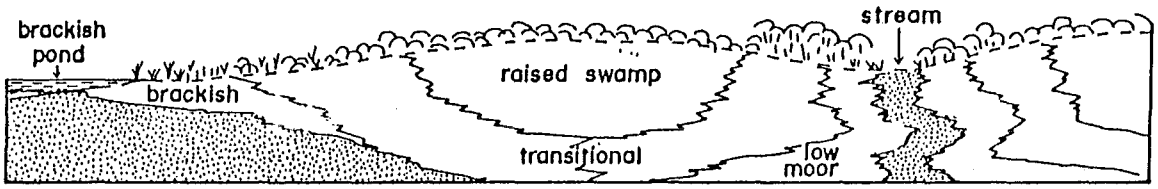


Figure 7.16 Diagrammatic representation of the principal swamp environments inferred for Upper Waimangaroa coals. From Newman, (1986).
A similar reconstruction can be applied to the Webb-Baynes Block at Buller Coalfield.

This model was applied specifically to the Upper Waimangaroa area, and tentatively to the mining areas further west (Sullivan Mine-Mt Frederick area), which may have occupied the western margin of the same basin. Uninterrupted extension of the basin to the Stockton-Webb area seems probable, but this cannot be ascertained until further study of the intervening areas is carried out.

(b) The Webb/Baynes area. Lithostratigraphic evidence from closely spaced drillholes (100-200m apart), coal analyses and coal petrography enabled Newman (1985a) to recognise the interaction of a peat swamp environment with a peripheral environment of very low energy, possibly lagoonal, mud accumulation. Gradual transgression from east to west is envisaged to have drowned the swamp in low-lying areas, depositing mud or muddy coal, whereas in more elevated swamp areas, peat accumulation survived without mud contamination until overwhelmed by fluvial sands. A continuous range of swamp type is recognised, from high-moor, through low-moor, to lacustrine or lagoonal deposits which form broad, linear barren zones of highly carbonaceous mudstone.

An Al_2O_3/SiO_2 graph for Webb/Baynes drillcore samples (Figure 7.17) shows a strong concentration about a point on the kaolinite line, near the 100% boundary. However, to assume that many samples have a mineral assemblage which is almost entirely kaolinite is incorrect, for as will be shown below, the highly kaolinitic Al_2O_3/SiO_2 ratio is largely a result of illite-boehmite mixtures accompanying kaolinite. It is known that some boehmite-bearing composites contain traces of quartz, and some quartz-bearing composites contain minor boehmite, probably as a result of mixing of discrete mineralogical horizons within the composite interval. However, some of the quartz may represent down-hole contamination of the sample by grains from the overlying quartzose sandstones, despite the care taken to avoid this. In view of the extremely low ash values for some coals, very small amounts of contamination would have a major effect on mineral matter composition.

The very thick seam of ultra-low ash coal in the Webb/Baynes Block (>10m at 0.2% ash in some profiles) implies unusual swamp conditions at the time of peat accumulation. Extreme examples of high-moor, low ash peat have been considered to be modern analogues of low ash coals.

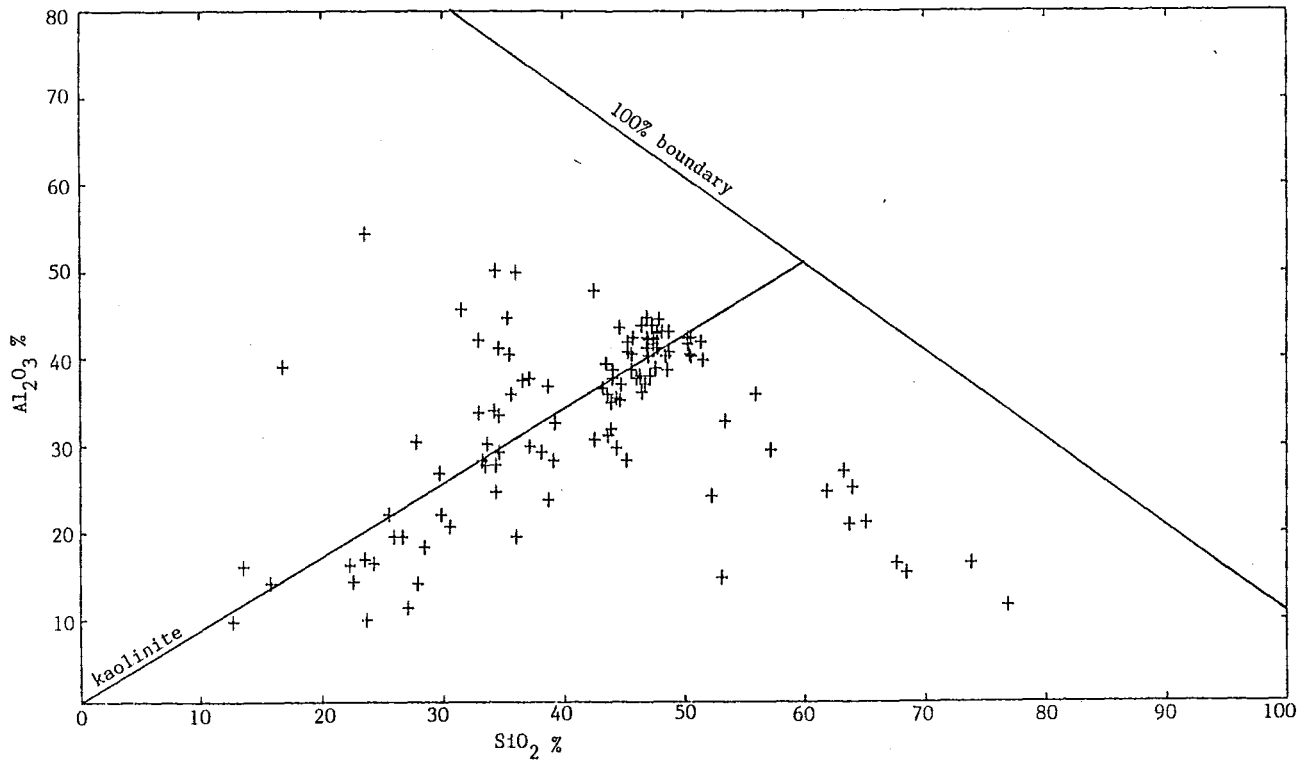


Figure 7.17 Al_2O_3 vs SiO_2 for Webb/Baynes coals, Buller Coalfield.

Bogs of this type are dome-shaped, or if extensive, flat-topped with convex margins. By maintaining their own water table, they are able to stand several metres above the regional water table or drainage areas, and thereby inhibit the influx of sediment-laden floodwaters. Elevation of the peat also tends to stabilise drainage channels and restrict their migration, enhancing uninterrupted accumulation of low ash peat (Teichmüller, 1962; Teichmüller and Teichmüller, 1982; McCabe, 1984). A paucity of nutrients also contributes to the low ash character of peats originating in raised bogs, which are dominantly ombrotrophic (rain-fed). However, leaching processes are also significant in reducing the mineral matter content of raised-bog peat (McCabe, 1984); these processes are favoured by good drainage (Keller, 1956; Moore, 1968), and low pH (Cecil et al., 1980; McCabe, 1984).

Unfortunately, the detailed petrographic study by Newman (1985a) did not produce independent evidence of bog pH, although good drainage was implied on the basis of anomalously low volatile matter values for coals attributed to a raised-bog origin. Poor tissue preservation was considered to result from microbial decomposition in "relatively well drained, well oxygenated" bogs, although an absence of inertinite showed that advanced oxidation did not occur.

The presence of boemite in low-ash Webb/Baynes coals attributed to raised-bog peats is good evidence for strong leaching during peat accumulation. The small amount of mineral matter present in the low ash coals may have entered the swamps as fine, suspended sediment during flood episodes, or may represent wind-blown material from nearby lagoonal areas. Some swamp areas experienced brief periods of lagoonal flooding, as demonstrated in the Webb Opencast (1984 face) where a 1m band of sheared carbargillite was found to comprise almost 90% illite (B26, Table 4.3).

More persistent flooding at the margin of the barren belts has resulted in finely interbedded coal and carbonaceous mudstone, e.g., sample B27, which shows a kaolinite-illite-boehmite assemblage in both floats and sinks. Quartz is absent. An in situ leaching origin for boehmite in the barren belt lithologies is incompatible with Newman's (1985a) interpretation of these zones as areas of standing water at the margin of the swamp. Alternatively, a transported origin must be invoked, as discussed for boehmite in Greymouth Brunnerton coals. Once again, there is little evidence of aluminous fossil soils or kaolinitic deposits, and aluminium hydroxides are restricted to the coals and barren belt sequences. Inertodetrinite is virtually absent. Occurrence of boehmite-bearing, low ash coals of probable raised bog origin in juxtaposition to the barren belts strongly suggests that aluminium was leached from the raised bogs, transported in solution or as a colloid, and precipitated in nearby drainage areas in response to higher pH (Figure 7.18).

Derivation of aluminium hydroxide by transport in solution can be expected if the bogs were strongly acid. Studies of modern peat show that the pH of a zone extending down 1-2m below the surface of high-moor swamps can fall below 4, particularly if Sphagnum species are present (Waksman & Stevens, 1929; Teichmüller & Teichmüller, 1982). Although there is no paleobotanical evidence regarding the presence or absence of Spagnum, the concept of acid leaching in high-moor bogs is an attractive theory for removal of both silica and alumina from the Webb/Baynes peats, thereby leading to the extremely low ash values observed for coals.

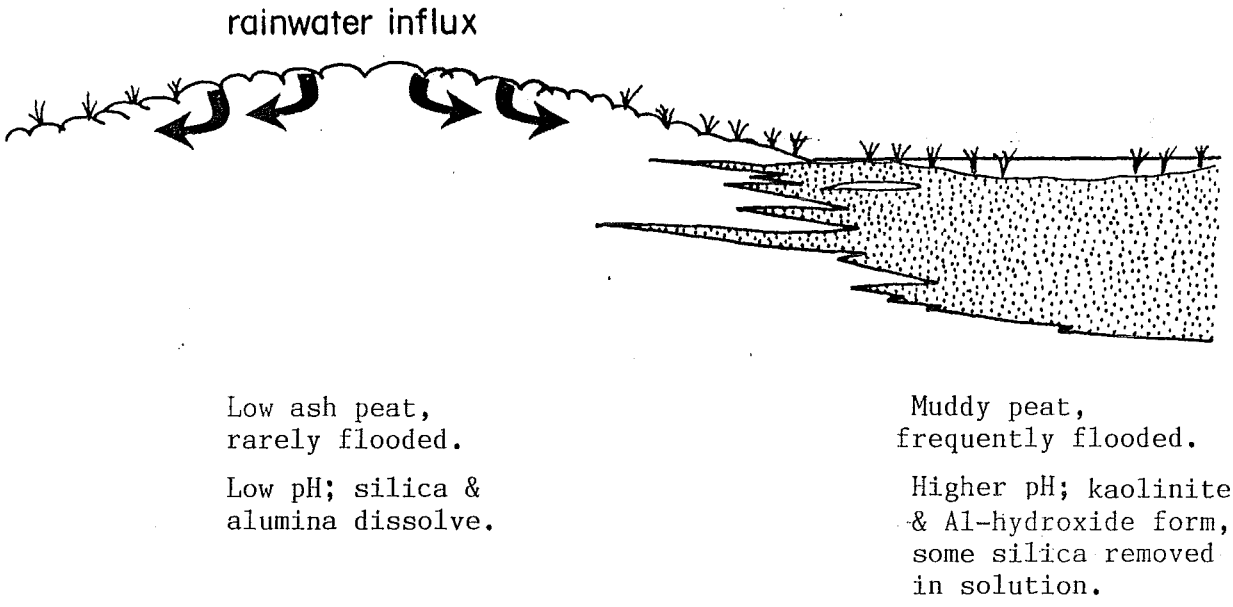


Figure 7.18 Model for simultaneous origin of ultra-low ash coal and high ash, boehmite-rich barren belt at Webb/Baynes area, Buller Coalfield.

Swamp water entering the more stagnant, flooded, less acid barren belt areas would deposit kaolinite, and surplus aluminium would polymerise and precipitate. Free quartz, which is lacking in the barren zones, has probably been removed by diagenetic reaction with introduced aluminium species to yield kaolinite. Sink-float data for the barren belt samples show a very similar ash composition for both sinks and floats at S G 1.36, demonstrating a very uniform distribution of clay minerals throughout this material, consistent with an authigenic origin for at least some of the components.

To investigate mineralogical trends accompanying environmental change, a set of 4, 0.6m plies from drillhole UG4, Webb-Baynes Block, were analysed. These plies span a transition zone where very low ash coal mid-seam gives way to high ash coal near the seam roof (Figure 7.19). Surprisingly, boehmite is present in all plies, even where ash values exceed 20%, suggesting that either the flooding of the roof peat alternated with periods of leaching, or aluminium in solution was supplied by laterally coexisting high-moor bogs, where transgressive flood-

ing had not yet occurred. Newman's (1985a) model of depositional history, whereby flooding was gradual and persistent, supports the latter interpretation. An independent test based on geochemical or mineralogical data is difficult to apply.

From ply 6 upwards, the increase in ash indicates substantial flooding resulting from a change in environmental regime. Highest values for kaolinite, boehmite, TiO_2, and P_2O_5 all appear in ply 7 (29/937), immediately beneath this high-ash roof zone. This is interpreted as marking a critical transition from a nutrient-poor, oligotrophic high-moor bog to a wetter, less acid, eutrophic or minerotrophic setting. Sodium-in-coal values continuously decline upwards to zero, and no explanation can be offered for this depletion, which is too extreme to be explained merely by an increase in ash. Nickel-in-coal values increase with mineral matter, showing that nickel is largely inherited with sediment. This relationship is demonstrated by other Buller samples, which indicate around 30 ppm nickel in detrital mineral matter, and typically 0.5-3 ppm associated with the coal substance.

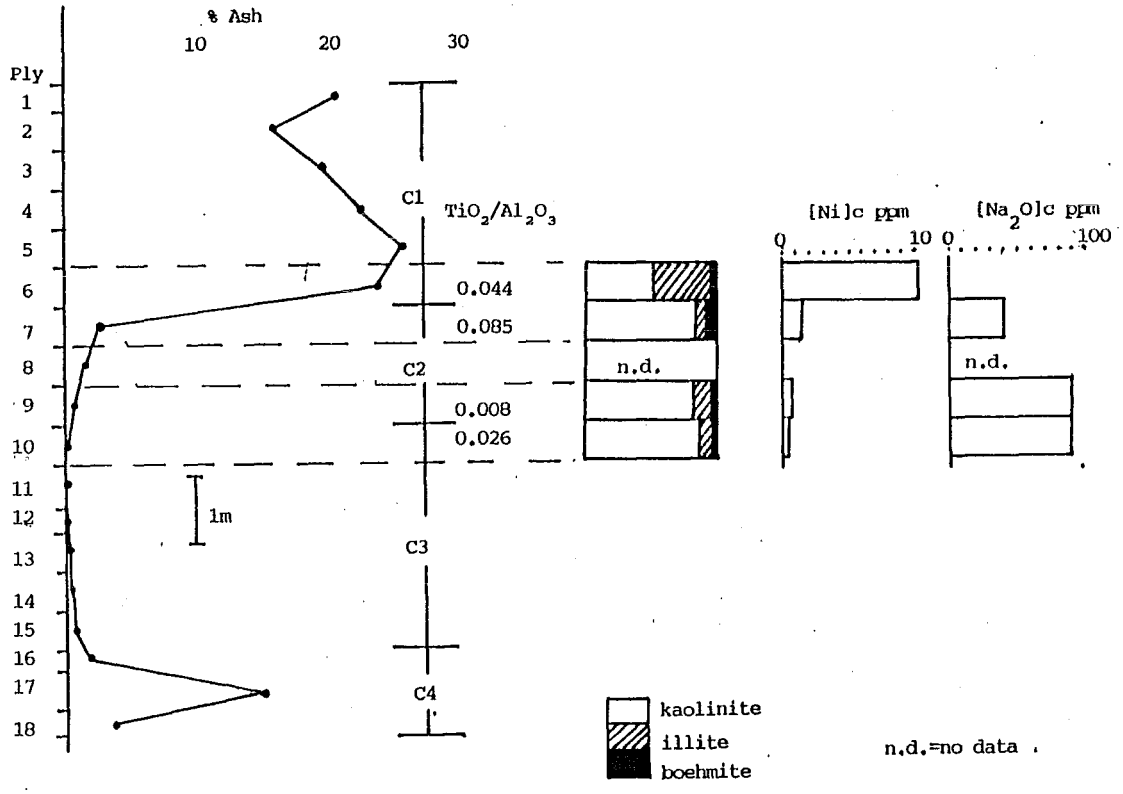


Figure 7.19 Nickel and sodium values in whole coal, TiO_2/Al_2O_3 ratios, and silicate mineralogy, for 4 plies over a low ash - high ash transition zone, Webb/Baynes drillhole UG4. C1 - C4 are composite intervals.

Minor mineral components in Webb/Baynes coals are sparse in comparison to kaolinite and illite, as might be expected from leached, nutrient-poor peats. An exception to this is pyrite, which may be largely post-burial in origin (Newman, 1985a). Neither crandallite nor carbonate minerals were identified. Rutile was detected in a few samples, and appears to be common in the barren belt carbargillite. It may have several possible origins, as discussed for rutile noted in illite-rich Brunner coals at Greymouth Coalfield.

The Buller samples are the only West Coast coals known to contain more than trace amounts of chlorite. The occurrence of this mineral in coal is considered rare (e.g., Mackowsky, 1982), and its paucity attributed to ease of weathering in acid leaching environments (e.g., Gluskoter, 1967; Weaver and Pollard, 1973; Rao et al., 1979). The Buller chlorite in extremely low ash, boehmite-bearing coal cannot be considered detrital, and an authigenic origin is discussed in the following chapter.

(c) Other areas of the Buller Coalfield. Extremely low ash coals in areas other than Webb-Baynes are generally of limited extent, and rarely exhibit a strongly hyperaluminous character. Run-of-mine samples from the Sullivan, Escarpment, and Charming Creek Mines all contain mineral matter which is dominated by kaolinite, but quartz is also present and no boehmite was detected. However, a more recent sample from the Sullivan Mine (37/040) contained boehmite and lacked quartz, and must be assumed to have come from a different working area. Hyperaluminous coals probably occur in numerous "patches" thoughout the Buller Coalfield. Gray (1981) has drawn attention to the alumina-rich ash for drillcore samples from the Cooks Lease area, which lies on the extreme north-eastern margin of the Upper Waimangaroa Sector.

Data for 119 drillcore samples from the Upper Waimangaroa Sector have recently become available, although no samples have been analysed mineralogically. Al_2O_3/SiO_2 relationships for these coals (Figure 7.20) show a more siliceous trend than do the Webb-Baynes data (Figure 7.17). Fewer Upper Waimangaroa samples plot above the kaolinite limit, and substantial scatter below this line indicates the influence of quartz.

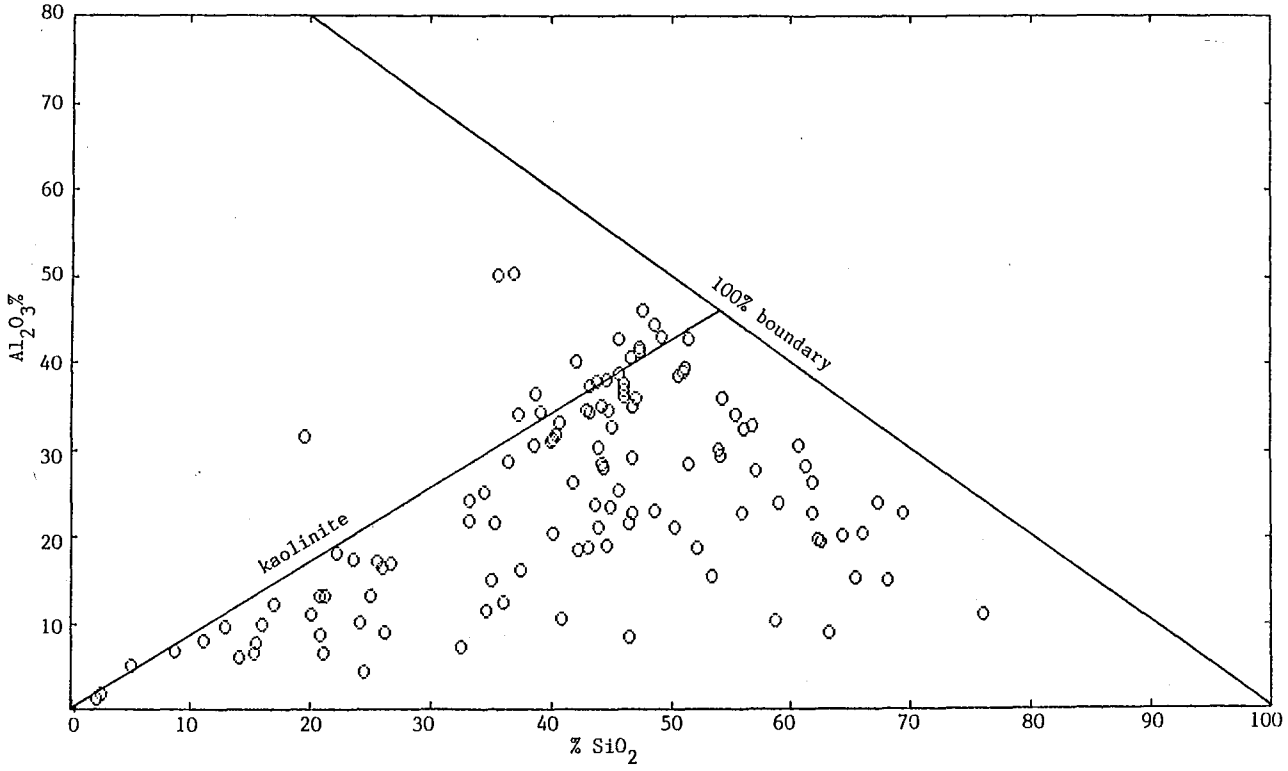


Figure 7.20 Al_2O_3 vs. SiO_2 for Upper Waimangaroa Sector coals, Buller Coalfield

Newman (1986) describes the occurrence of sporadic quartz grains in some of the "brackish-influenced" coals, which suggests rafting of debris in lagoonal waters.

Ash and sulphur measurements, ash constituents analyses, and computed mineralogy (Table A2.8, Appendix 2) indicate considerable variability for these coals. Newman (1986) demonstrates that a general increase in ash from east to west corresponds to an increase in relatively low-moor, sometimes brackish swamp character, based on an interpretation of coal type and proximate analyses. Many of the high ash samples have a relatively large illite component, and probably represent persistent lagoonal flooding. High sulphur values, which range up to more than 10%, are attributed to both syndepositional and postdepositional enrichment; Newman (1986) was able to identify only local examples of syndepositional enrichment, and concluded that postdepositional influences were most significant, particularly in the case of thin seams enclosed by permeable fluvial sandstones.

Some coals of the Upper Waimangaroa Sector contain an unusual abundance of P_2O_5 and TiO_2 in ash. Although direct mineralogical data are not available, these components have been computed as crandallite and rutile respectively, by analogy with other Brunner samples. A comprehensive interpretation of the distribution of these minerals would require detailed analysis of the data, including drill logs, and a consideration of paleogeography; this has not been attempted. However, high-P_2O_5 compositions suggest the existence of either nutrient-rich swamps, or conditions which were highly favourable to phosphate fixation. Correlation between P_2O_5 and TiO_2 is poor. A comparison of TiO_2/Al_2O_3 ratios with those of the Webb-Baynes samples (Figure 7.21) shows significantly higher values in the Upper Waimangaroa case (Figure 7.22), although both sets of data exhibit considerable scatter. The difference between the two groups of data is assumed to reflect the less intense leaching of the Upper Waimangaroa peats.

7.5 OTHER BRUNNER COALFIELDS

West Coast coals outside the three main high rank coalfields already described were not examined in detail during the course of this project. Very little drilling or exploration has been carried out in the minor coalfields in recent times, and only a small number of ash constituent analyses are available for the coals from these areas. Nevertheless, geochemical and mineralogical features of these coals justify their inclusion in this chapter.

7.5.1 Reefton-Garvey Creek.

Several isolated blocks of Brunner Coal Measures in the Reefton area (Figure 4.7) represent parts of a single depositional basin in which the coal measures achieve a maximum thickness of more than 250m, and contain up to 6 separate coal seams at different horizons (Suggate, 1957). In the Garvey Creek area, swelling number reaches 4, but elsewhere, the coals are only weakly swelling.

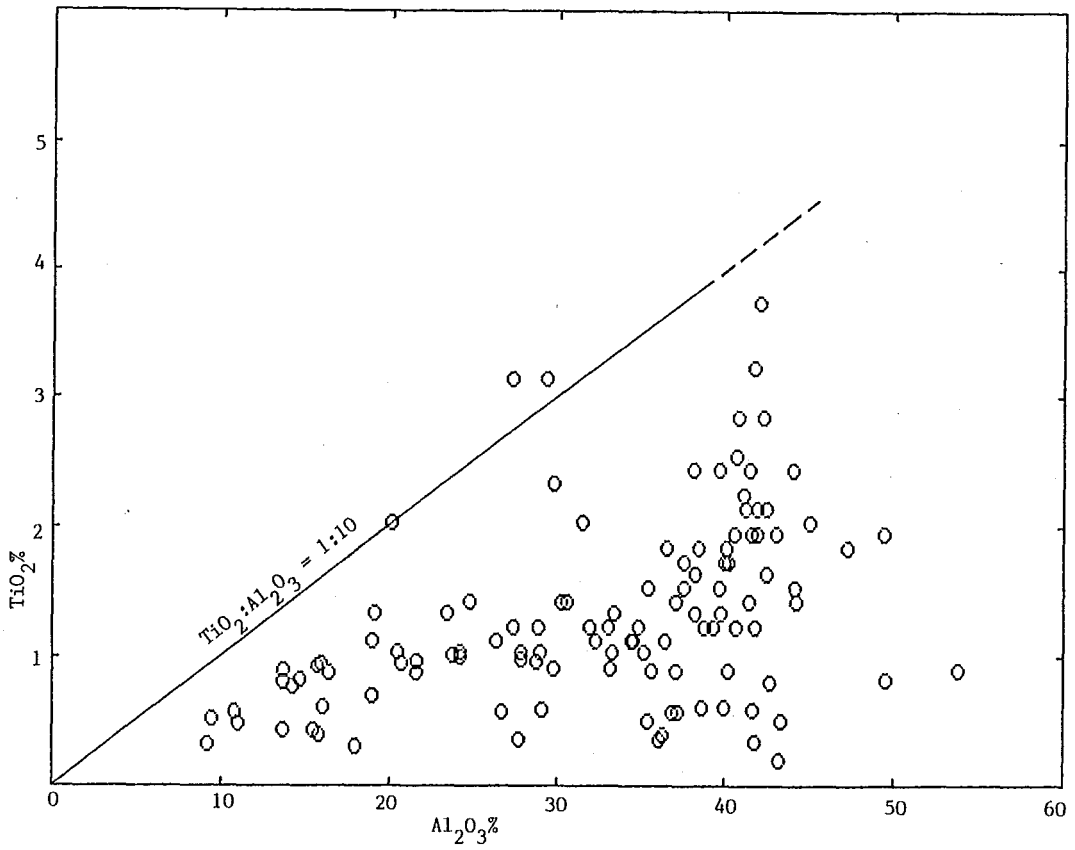


Figure 7.21 TiO_2 vs Al_2O_3 for Webb-Baynes coals, Buller Coalfield

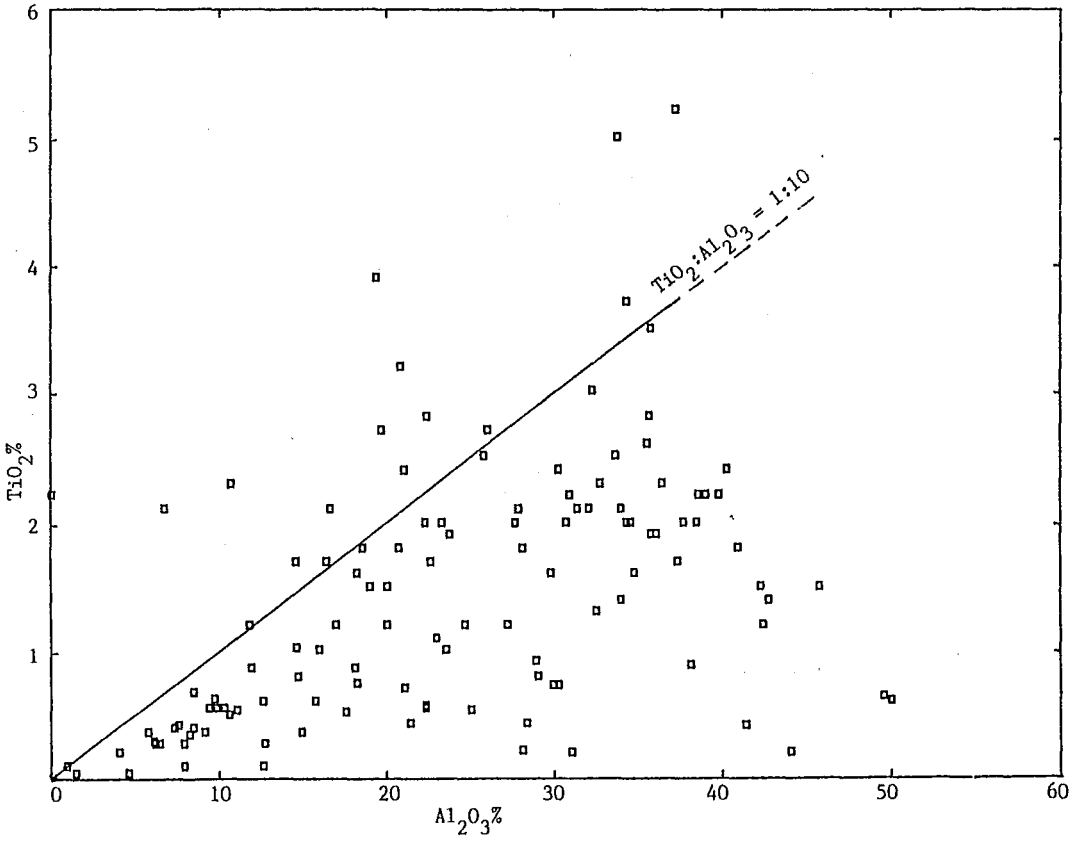


Figure 7.22 TiO_2 vs Al_2O_3 for Upper Waimangaroa coals, Buller Coalfield

Most current output from the Garvey Creek area comes from a state-operated opencast at a large outlier known as Island Block, where a thick basal seam is overlain by a sequence of sandstones and mudstones containing several thinner seams, which are occasionally thick enough to justify their recovery during stripping.

The Island Block outlier has been evaluated by the drilling of 4 holes, from which the writer obtained spot samples of coal cores. In addition, three ash samples of run-of-mine coal from the opencast were provided by CRA. One mineralogical analysis and three calculated assemblages indicate that quartz, kaolinite, and pyrite are all well represented in the main seam (Tables 4.3, 4.5). Two spot samples from the upper seams show a similar trend, but also contain an unusual abundance of phosphate minerals. Both samples contain crandallite, and one (B36) also contains apatite. The paragenesis of these two minerals is uncertain; the apatite may be detrital and crandallite an alteration product, as described from phosphate deposits by Altschuler et al. (1970). The apatite-bearing sample is distinguished by an anomalously low Sr/P_2O_5 ratio. Apatite and crandallite (goyazite) are known to occur in Australian coals (Cook, 1962; Ward, 1978), but there is apparently no record of both minerals coexisting in coal.

Carbonate minerals were not identified in the mineralogical analyses of the prepared LTA samples, but are known to exist in concretionary masses within the seams. Both XRD of the concretions and mineralogy computed from ash constituents shows dolomite to be the most abundant carbonate mineral present. When broken open, some concretions reveal an interesting paragenetic sequence of minerals. A carbonaceous, dolomitic groundmass hosts replacement veinlets of pyrite and marcasite, which replace core and rim zones of rare, subspherical masses of siderite (Figure 7.23). Whether dolomite replaced original siderite cannot be ascertained, but the siderite-sulphide relationship reflects postdepositional alteration of carbonate by sulphide solutions, as described by Smythe (1966).

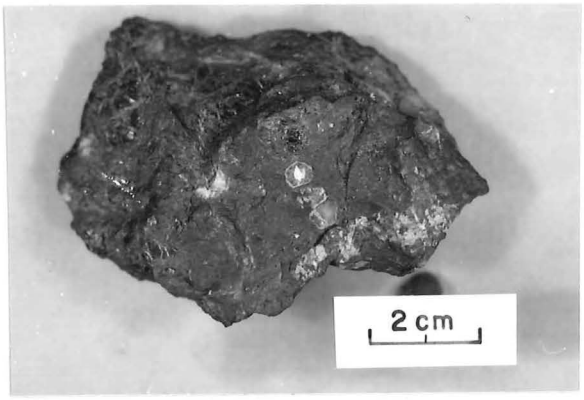


Figure 7.23 Carbonate-sulphide concretion from upper seams at Island Block, Garvey Creek. Blebs of siderite show rim and core replacement by pyrite and marcasite. Groundmass is dolomite.

The onset of marine conditions at Island Block appears to have been gradual, and in the absence of petrographic evidence, the extent of syndepositional marine influence on the seams remains unknown. The first definite marine indicators are found some distance above the uppermost seam. The upper seams are known to be sulphur-rich, and may have been influenced to some extent by brackish water in the peat swamps, but the entire coal measure sequence is sand-dominated and can be expected to have favoured deep circulation of marine water after burial. Abundant sulphide mineralisation has occurred at seam roofs, where both clays and quartz have been replaced (Figure 3.8f). Local formation of siderite in the peat indicates that there were some periods when marine influence was absent (Mackowsky, 1968).

Further north, run-of-mine samples from some of the North Reefton mines (Burke's Creek, Hyde, Dauntless) contain a mineral assemblage similar to that of the Island Block coals, except that dolomite is more abundant and illite appears to decline. One coal specimen from Burke's Creek Mine was found to be silicified; this characteristic is very unusual among West Coast coals, although some other occurrences are known from the low rank areas (see discussion in section 7.5.3).

High P_2O_5 values are restricted to the samples from the upper seams, and one run-of-mine sample, all from Island Block Opencast. Only the most recent run-of-mine sample (30/344) has this characteristic, possibly because of inclusion of coal from the upper seams, which were

not recovered during early operation of the mine. Therefore, the unusually phosphorus-rich coals in the area may be restricted to the Garvey Creek upper seams. Additional work is needed to identify the cause of these high phosphorus values. Source rocks may have provided an unusually rich source of nutrients; local basement lithologies include both fossiliferous, carbonate-bearing Devonian sequences (Reefton Group), and Triassic tuffs and volcanic conglomerates (Topfer Formation, Suggate, 1957). However, paleoenvironmental factors may be of greater importance. Similarities between the coal-bearing sequences at Island Block and Upper Waimangaroa can be identified, i.e., both areas contain phosphorus-rich coals which originated from swamps where there was probably some brackish water influence, and where minimal leaching occurred. A nutrient-rich environment may have been a common factor.

7.5.2 Flat Creek Coalfield.

An isolated remnant of Brunner Coal Measures at Flat Creek, southwest of Murchison, is commonly classified as part of the Murchison Coalfield, which incorporates several scattered deposits of both Eocene and Miocene coal measures. At Flat Creek, thin coal and thick coal measure sandstones pass laterally into thick coal, which is almost immediately overlain by thick carbonaceous mudstones. These mudstones are of uncertain depositional setting, but pass gradationally upwards into the marine Kaiata Mudstone. The coal is not currently mined, but remaining reserves are under evaluation for further production.

Mineral matter and ash constituents were analysed for a single face sample (B45) from an old opencast. The mineral assemblage is very similar to that observed for Island Block coals, comprising subequal proportions of quartz, kaolinite, and illite. Although there is no mineralogical evidence of strong leaching of the peat, the low ash value (1.6%) suggests very stable depositional conditions and restricted sediment supply. Paleogeography of the depositional environment is poorly known. Pyrite dominates the mineral matter, chiefly because detrital components are sparse. Some specimens of nodular carbonate from the seam were found to be ankerite, although this mineral does not appear in the analysed face sample. Concentrations of minor ash constituents are low, with the exception of P_2O_5, which is 0.82% in ash.

7.5.3 Low Rank Coals.

All West Coast coals described in the preceding sections are of bituminous rank. Several areas of sub-bituminous coal are mined, and some of these have been included in the study. All of the low rank coals are from Brunner Coal Measures or Rotokohu Coal Measures (Miocene, Figure 1.4).

Although the low rank Brunner coals are of very similar age to the bituminous coals at Reefton and Buller coalfields, the low rank samples have substantially different mineral matter characteristics. For simplicity, the low rank areas can be divided into coal deposits of the Buller-Inangahua area, and those located in the coastal strip between Greymouth Coalfield and Westport. No attempt has been made to obtain a systematic coverage of these areas.

All of the low rank coals are characterised by a high content of organically-bound calcium, which is converted to gypsum during the low temperature ashing process, thereby greatly retarding the oxidation rate. Most low rank samples could not be completely oxidised, necessitating special treatments to remove residual coal from the LTA prior to analysis.

From the Inangahua area (Figure 4.8), run-of-mine samples from Heaphy's, Fletcher Creek, and Burley's Opencast Mines have been examined. Of these, the Heaphy coal has the highest rank, and is the only coal known to contain mineral-bound calcium, which occurs as calcite. However, a large gypsum component in LTA suggests that only a small proportion of the calcium can occur in this mode. Quartz and kaolinite are the only natural minerals identified in samples from Fletcher Creek and Burley mines. These minerals are accompanied by illite in coals from Heaphy's Mine and Brighton Mine (Punakaiki Coalfield). Only the Heaphy and Brighton samples contain pyrite, but oxidation during mining or sample storage may account for the lack of sulphides in other cases. No combined forms of sulphur - ash constituent analyses are available, therefore the amount of pyritic iron in these samples cannot be calculated.

Johnston (1987) made a limited study of mineral matter in Rotokohu coals (Miocene), which are worked at several localities near the Fletcher Creek and Burley opencasts on the west side of the Inangahua River. Johnston's work shows that abundant organically-associated calcium and magnesium are present, and that particulate mineral matter is dominated by quartz, and to a lesser extent, kaolinite. Illite, pyrite, and rare feldspar are chiefly restricted to carbominerites. However, a prominent mineral characteristic of Rotokohu coals is the presence of silicified horizons.

Previous work by Blattner (1976) and Soong and Blattner (1986) had described the occurrence of authigenic quartz in coal from the McLaughlin Opencast at Charleston, where idiomorphic quartz crystals up to 4 mm in length occur in thin lenses near the middle of the seam. A biogenic silica source was suggested, although no evidence could be found to support this concept. The crystal horizons contrast sharply with the face sample (B49, this work), which is extremely low in silica and suggests loss of this component from the peat. The occurrence of quartz crystals in thin (5 cm) beds, and the description of etch pits on crystal faces suggest a near-surface origin.

In the Rotokohu coals, authigenic quartz forms prominent beds, typically 5-20 cm thick, in the coal seams. On a microscopic scale, quartz can be seen to both infill and replace maceral structure. The silicified horizons occur in association with, and in some cases grade into, coal rich in detrital quartz (Johnston, 1987). This suggests that local remobilisation and recrystallisation of silica has occurred, either as a result of substantially raised pH (>9), or by the localised action of organic complexing (Bennet and Seigel, 1986).

The standard Brunner calculation method has been applied to the few ash constituent analyses obtained for the low rank coals, to obtain the mineral assemblages appearing in Table 4.5. Many of these mineral totals must be regarded as invalid, because the mineralogy of the inorganic components differs from that of the bituminous coals. A large proportion of the sodium, potassium, calcium, magnesium, and possibly iron and aluminium, may be organically bound. Charleston, Fletcher Creek, and Heaphy samples were analysed for water-extractable and

ammonium acetate-extractable alkalis, using a conventional procedure described by Black (1982). Two bituminous coals were included for comparison. The results of these analyses (Table 7.2) show that only about one-third of the calcium in the low rank samples is exchangeable, in contrast to sodium, which is almost completely exchangeable. Extractable potassium is intermediate (60-80%), and may originate, at least in part, from clay minerals.

The Fletcher Creek coal has a hyperaluminous ash composition, leading to the calculation of a boehmite component in Table 4.5. However, this mineral cannot be detected in LTA, and the "surplus" aluminium may be organically bound. Whether this aluminium originated in the peat swamp or during some subsequent stage, cannot be determined on available evidence.

Coal from Heaphy's Opencast contains the highest sodium values observed for any currently mined West Coast coal (Table A2.2; Newman, 1987b). The unusually high sodium content, which ranges up to 10% in ash and 0.35% in whole coal, cannot be attributed to any known mineral occurrence. More than 80% is leachable or acetate exchangeable (Table 7.2). CRA records show that chlorine in Heaphy coal is below detection limit (0.02%), indicating that less than 10% of the sodium can be present as chloride. Present evidence does not permit any satisfactory explanation of the high sodium content of this coal.

No mineral analysis has been given for the Charleston coal, which is overlain by recent gravels at McLaughlin's Opencast, from which a run-of-mine sample was found to be contaminated by sand. A heavy liquid sink fraction of this coal showed coarse grains containing fresh feldspar and other granitic debris which almost certainly came from the overburden. An uncontaminated 2m face sample from mid-seam was used for the chemical analyses (B49, Tables 7.2 and A2.2); CaO, MgO, and sulphate comprise the main ash components. After removal of synthetic and soluble components from LTA, insufficient mineral matter remained for XRD analysis. If the "true mineral" portion of the ash is assumed to consist of SiO_2, Al_2O_3, K_2O, and TiO_2, a theoretical detrital ash value of only 0.16% is indicated. It is apparent that this face sample did not include any of the authigenic silica bands described above.

Sample	ANALYTES IN WHOLE COAL PPM									
	Water extractable			Acetate extractable			Total analyte*			Max. Sulphate Ca [2]
	Na	K	Ca	Na	K	Ca	Na	K	Ca	
Charleston CHN-2	38	6	45	130	45	2065	150	60	6200	250
Fletcher Ck B48	25	<2	144	80	45	2030	76	71	7060	340
Birchfields (1982) B1	62	<2	98	73	3	-[3]	135	6	689	<10
Heaphy 27/507	370	3	4	1960	43	1730	2770	75	5380	
Strongman (P20)	5	<2	4	33	4	10	180	167	81	
Sullivan 27/511	28	<2	105	33	2	110	150	245	350	

*Total analyte in whole coal, as computed from ash analysis and ash yield.

Na values for this column: LTA/borate fusion/flame photomtr. for Fletcher Ck and Sullivan samples, HTA/XRF for others.

[2]Maximum Ca which could be present as sulphate.
[3]Not measured due to procedural error.

§Samples: Heaphy & Sullivan CRA ROM. Fletcher Ck privately sampled ROM, others are spot samples.

Table 7.2 Acetate-extractable alkalis in selected West Coast coals.

7.6 SUMMARY

7.6.1 Quartz-Kaolinite-Illite-Boehmite Variation

The common occurrence of boehmite in Brunner coals requires a 4-component variation diagram to demonstrate fields and trends defined by the major aluminosilicate minerals. Computed mineral data have been plotted on diagrams of this type for each of the Brunner deposits described in this chapter (Figures 7.24, 7.25). Although the fields defined by the points for each deposit may be influenced by source composition and the extent of alteration outside the swamps, the variation patterns are considered to be strongly controlled by depositional environment within the swamps.

Paleocene Brunner coals from central Greymouth Coalfield provide an extreme example, by reason of their extended swamp history. Points plotted for these coals fall along the kaolinite-boehmite boundary, with the exception of some high-ash, illite-rich specimens. The Eocene coals from this area are less aluminous, and plot almost entirely within the QKI triangle.

An opposite extreme is presented by the pattern for Pike River Brunner coals, where minimal leaching and a probable influence from rafted grains restricts most of the points to the QKI triangle, with a strong bias towards quartz.

Intermediate trends are exhibited by samples from the Webb-Baynes Block and Upper Waimangaroa Sector. Of these two sets of data, the Webb-Baynes points are clearly the most hyperaluminous and plot almost equally in both the quartz and boehmite triangles. A crowding of points near the middle boundary is apparent, although this concentration is substantially dispersed by kaolinite-illite variation. This dispersion, and the wide scatter of the points generally, indicates that substantial environmental variation exists within a comparatively small area (approx. 250ha). Many of the Webb/Baynes samples contain significant amounts of chlorite, which is not incorporated in the mineral calculations. The chlorite aluminosilicate components would be calculated chiefly as kaolinite. Similarly, some samples may include potassium-bearing sulphates,

leading to an overestimation of illite. Two extremely potassic samples have been eliminated from the plot for this reason.

The scatter of points is more extreme for the Upper Waimangaroa pattern, where a larger range of depositional environments is represented. Displacement of the field towards the quartz apex may be due, in part, to the influence of rafted grains. Unlike other Brunner coals, the Upper Waimangaroa field shows some very illite-poor compositions which resemble those exhibited by "low water table" Paparoa coals.

Figure 7.25 shows the plotted range of compositions for samples from the minor coalfields, and also some miscellaneous samples from the high rank areas. Tied points represent compositions for density fractions from the sink-float samples. It is notable that the proportion of illite shows very little change in these fractions, whereas other components show a continuous change to increasingly aluminous compositions.

One Webb Opencast run-of-mine sample is so quartz rich in comparison to the remainder of the Webb-Baynes compositions that contamination from the sandstone overburden is suspected. This suspicion is reinforced by the high iron content of the sample (30/349), which suggests inclusion of a large proportion of pyritic seam tops, where contamination from overburden stripping is worst.

7.6.2 Sulphides and Carbonates

No attempt has been made to quantitatively assess sulphide mineral distribution; such an assessment would require full-seam intersections of unweathered coal, which are not available for all areas. From the existing data, it is evident that sulphide abundance shows extreme variability between and within different Brunner coals. A marked increase in sulphide in seam roofs is common to every deposit, particularly where permeable roof rocks have promoted post-depositional sulphur enrichment. Because Brunner sulphide is almost entirely neoformational in origin, the coals often show a broad inverse correlation between pyrite, as a proportion of total mineral matter, and ash. The sporadic occurrence of marcasite does not appear to be characteristic of any one deposit.

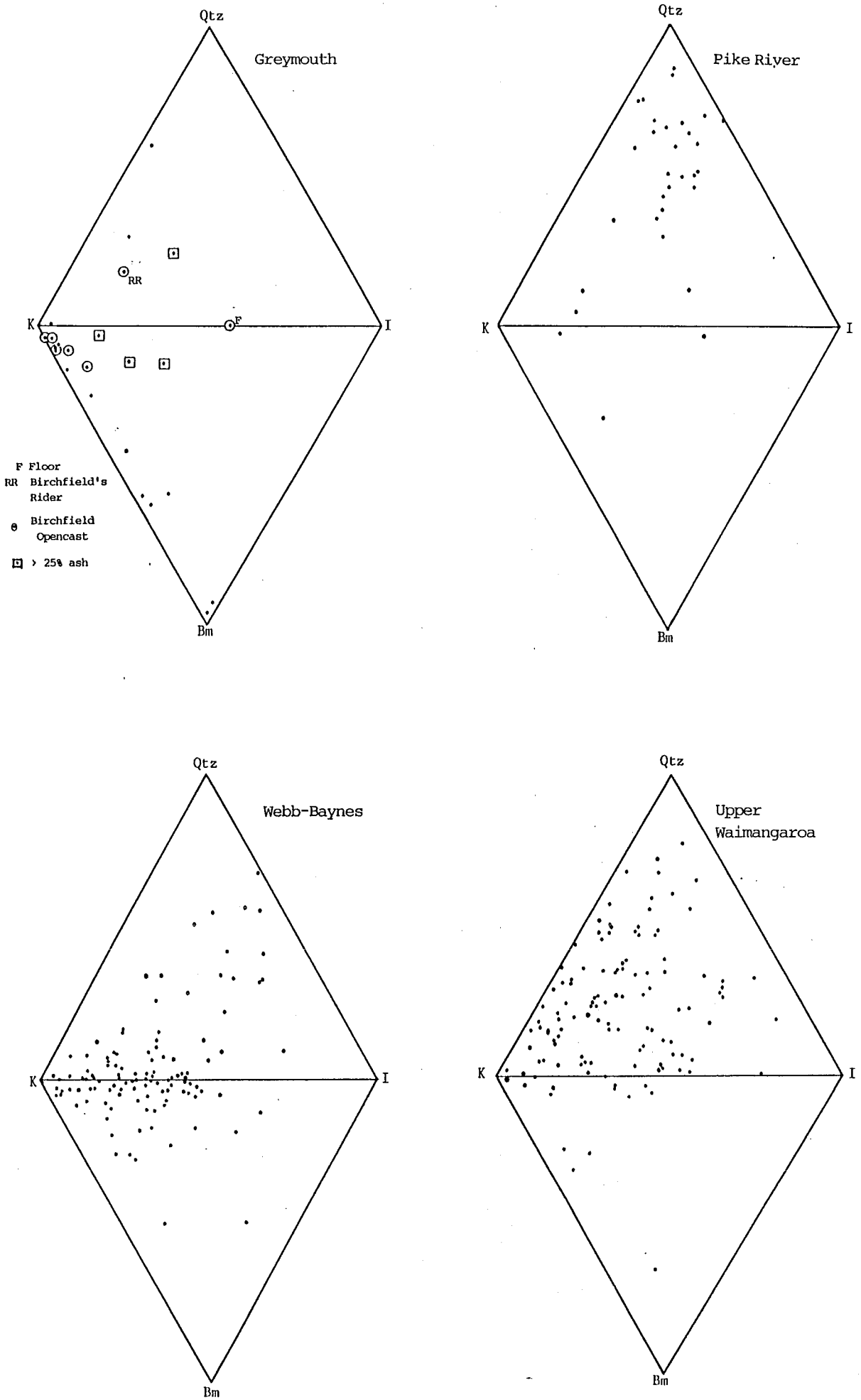


Figure 7.24 Quartz-kaolinite-illite-boehmite variation diagrams for four main high-rank Brunner coal deposits.

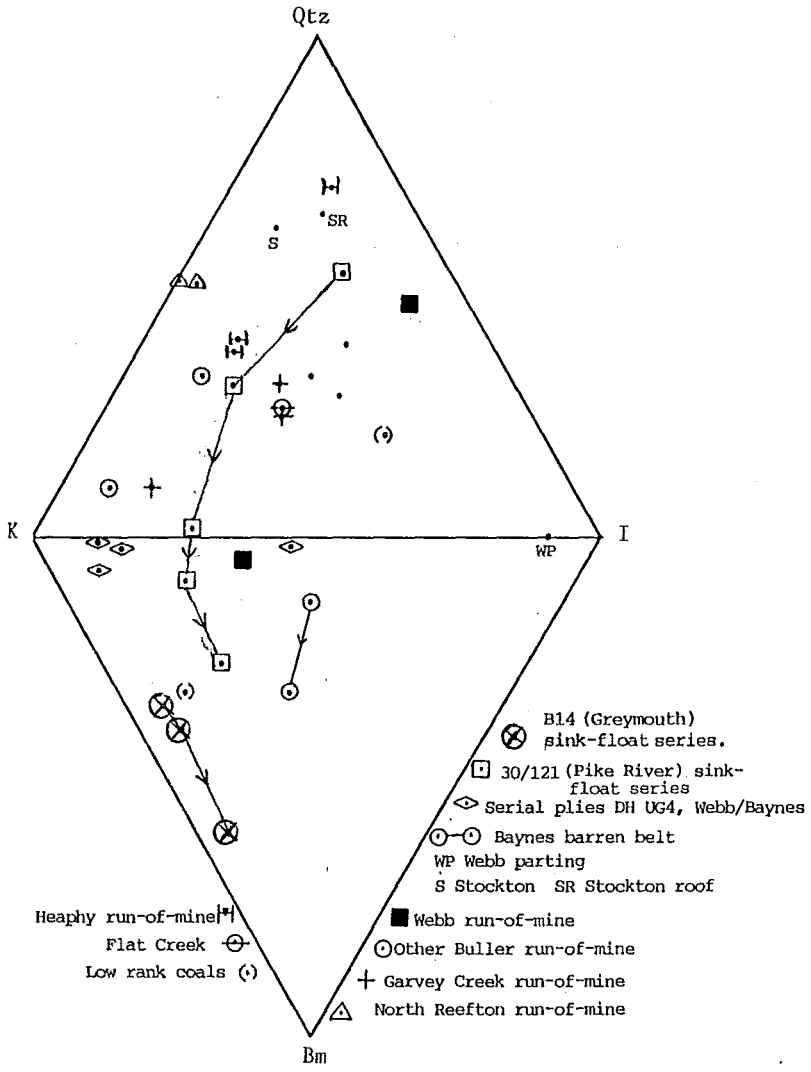


Figure 7.25 Quartz-kaolinite-illite-boehmite variation diagram for miscellaneous Brunner coals from both high rank and low rank deposits. Positions occupied by the low rank coals do not reflect their true mineral assemblage. Arrows between tied points show the high ash to low ash trend for sink-float fractions.

In contrast, calcite and dolomite show a greater uniformity within individual deposits, and a more clearly defined regional variation. Carbonates are poorly represented at Buller Coalfield, and also in the sub-bituminous coals where much of the calcium and magnesium may be organically bound. Coals at Reefton-Garvey Creek and Pike River contain both syngenetic and epigenetic carbonate, whereas at Greymouth, the Brunnerton coal contains epigenetic calcite, aragonite, and dolomite, which accompany "organically associated" dolomite. The Brunner seam at Pike River is outstanding with respect to a high abundance of carbonates, chiefly dolomite.

Siderite in Brunner coal appears to be restricted to rare cores of dolomite nodules at Garvey Creek, and nodular, syngenetic ankerite occurs only in the Flat Creek coal.

No simple pattern of paleoenvironmental control on the formation of syngenetic carbonates can be recognised. In particular, it is difficult to explain why some seams, which are known to be strongly marine-influenced, lack these minerals.

7.6.3 Titanium and phosphorus

To eliminate the obscuring effect of authigenic carbonates and sulphides, systematic variations in TiO_2 are examined by computing TiO_2/Al_2O_3 ratios. This has been achieved, in effect, by plotting TiO_2 against Al_2O_3 for Webb/Baynes and Upper Waimangaroa coals (Figures 7.21, 7.22).

All Brunner coal deposits show a very large variation in TiO_2/Al_2O_3 ratio. Although this variation is not readily explained, two trends can be discerned:

(i) For Greymouth, Pike River, and Buller coalfield samples, the lowest TiO_2/Al_2O_3 ratios coincide with boehmite in mineral matter, except in the case of high ash samples.

(ii) High TiO_2/Al_2O_3 ratios occur in situations where only moderate leaching can be inferred, and where brackish water may have sporadically influenced the accumulating peat, e.g., parts of the Upper Waimangaroa area, and Reefton-Garvey Creek Coalfield.

Although unusually high phosphate values tend to be associated with areas identified in (ii), above, correlation of P_2O_5 with TiO_2 is poor. Whereas most of the phosphate-rich Upper Waimangaroa coals are not boehmite-bearing, some ultra-low ash, hyperaluminous Webb/Baynes coals exhibit relatively high P_2O_5 in ash. Similarly, crandallite can be detected in the mineral matter from some of the boehmite-rich Brunnerton coals at Greymouth Coalfield.

7.6.4 Sodium in Whole Coal

Controls on sodium distribution in Brunner coals are obscure. Na_2O in ash against reciprocal of ash has been plotted for the main high rank Brunner deposits (Greymouth, Pike River, Webb-Baynes, and Upper Waimangaroa) in Figure 5.21. The slope of a line between any plotted point and the origin provides a measure of sodium in whole coal. In comparison to Paparoa coals, many Brunner coals contain very little sodium. An exception to this observation is found in the Greymouth and Pike River coals, some of which contain more sodium than any other West Coast coal except the anomalous Heaphy example. For the Greymouth Brunner coal, the abundance of free alumina is probably the cause of "fixation" of sodium in the coal as dawsonite, but other, unknown, factors are responsible for the introduction of the sodium into the seam, and retention of this alkali until reaction with alumina took place. Moderately hyperaluminous coals from Upper Waimangaroa and Webb-Baynes deposits show no sodium enrichment of this magnitude.

Some Pike River Brunner coals also show a high sodium content, but no dawsonite has been detected, and the few hyperaluminous coals are not among the sodium-rich group. Sink-float fractions for this coal show that sodium maintains a strong organic assocation (Table 5.2).

Unlike Paparoa coals, high-sodium Brunner samples show no correlation with mixed layer illite-smectites. The Brunner illites tend to be highly "stripped" of cations other than potassium, particularly where intense leaching is inferred; illite-rich horizons from the Webb/Baynes block exhibit Na_2O:K_2O ratios as low as 1:150 (Table 5.4).

7.6.5 Strontium

Strontium in Brunner coals appears to occur in three different modes, as follows:

(i) In crandallite. All P_2O_5-rich ashes exhibit high strontium values. The Island Block specimen containing apatite (B36) shows an anomalously low Sr/P_2O_5 ratio when compared with other samples which contain crandallite alone.

(ii) In carbonate minerals. Low-phosphate, calcium carbonate-

bearing samples from Greymouth Coalfield also have a high strontium content. The highest value recorded for West Coast coals (1.03% Sr, B20) coincides with an occurrence of aragonite. However, Sr/CaO ratios for carbonate-rich, phosphate-poor Pike River Brunner coal are low. The density fractions for Pike River sample 30/121 (Table 5.2) confirm that strontium does not substitute calcium in carbonate minerals in these coals; instead, an organic association is indicated.
(iii) Organic association. Most sub-bituminous samples exhibit high strontium values for which no mineral association can be recognised. The example from Pike River, described above, suggests that this characteristic may extend to some bituminous coals.

7.6.6 Nickel

Nickel-in-coal values for Brunner samples appear to be chiefly associated with illitic sediment, as shown by Figures 7.12 and 7.19. However, an organic association is also present, as demonstrated by nickel-in-ash values generally, and by the sink-float fractions (Table 5.2). Although no complete seam profiles have been analysed in detail, post-depositional nickel enrichment does not appear to have affected the seams. "Marine influenced" coals are particularly low in nickel, demonstrating negligible contribution of nickel by sulphide minerals. Buller coals attributed to high-moor bogs are also nickel-poor; the lowest values recorded from West Coast coals are those from the low ash plies, DH UG4, which contain approximately 0.5 ppm nickel (Figure 7.19).

CHAPTER 8

SUMMARY, CONCLUSIONS AND APPLICATIONS

8.1 SUMMARY

8.1.1 Mineral Assemblages

Mineral matter in coal from Paparoa Coal Measures and Brunner Coal Measures shows an extremely wide variation in chemical composition and mineralogical character. Much of this variation can be related to differences in depositional environment.

Paparoa coals contain a syndepositional mineral assemblage which is dominated by various proportions of quartz, kaolinite, and illite, accompanied by minor crandallite and rutile. The illite is commonly micaceous in character, but occasionally shows weak to moderate random interlayering by expandable clay. Abundant siderite and lesser amounts of other carbonates, all of postdepositional origin, are common in all Paparoa coals. Abundance and distribution of carbonate minerals appear to be related to permeability of interseam sediments. In some Paparoa coals, deep circulation of groundwater from overlying marine rocks has altered siderite to marcasite and pyrite, especially where the intervening lithologies are thin, permeable, and lack coal.

Mineral matter in Brunner coal exhibits some strong regional distinctions. Several of the Brunner mineral assemblages contain boehmite, kaolinite, and illite, but lack quartz, and are attributed to intense or prolonged leaching of the peat swamps. At Pike River Coalfield the Brunner seam contains abundant dolomite and calcite, but elsewhere these minerals are minor components. Pyrite is very widespread in Brunner coals, where it is concentrated in the top of the seams, chiefly as a result of postdepositional enrichment processes. Rutile, crandallite, chlorite and rare apatite occur as minor minerals, and dawsonite is locally abundant in alumina-rich Brunner coal at Greymouth Coalfield.

8.1.2. Influence of source and paleoenvironment

(a) Paparoa Coals The influence of different source rocks on mineral matter in Paparoa coals is poorly defined, and is heavily obscured due to controls exerted by the depositional environment. Volcanic rocks extruded during deposition of the Morgan Member, and possibly reworked during lower Rewanui time, may be responsible for high titanium and phosphorus values in some Paparoa coals, but high concentrations of these components also occur in situations where no volcanic influence can be identified.

Tectonically stable swamp areas, uncontaminated by flood sedimentation, have resulted in relatively inertinite-rich and subhydrous Rewanui coals, with very low ash and kaolinite-rich mineral matter. Rewanui coals attributed to high water table swamps on the basis of petrographic evidence are characterised by an abundance of quartz, which is at least partly derived from sediment rafted on floating vegetation. Seams representing extreme high- and low-water table swamps show some clear mineralogical and chemical distinctions, but less extreme examples are poorly differentiated by a comparison of whole seam data, and may represent the combined effects of environmental change during swamp history. Ratios of quartz, kaolinite, and illite, and the abundance of phosphorus, titanium, and possibly sodium, appear to be the principal distinguishing characteristics associated with contrasting swamp types.

Coals from the Dunollie Member are relatively inert-rich, and represent particularly low water table swamps which were influenced by low-energy flooding, good drainage, and regular aeration, producing extremely kaolinite-rich mineral matter.

The effects of leaching in Paparoa swamps may be estimated by comparing mineral matter and fine-grained lacustrine sediment. The sediment exposed to the swamp environment has lost all chlorite, gained kaolinite relative to quartz and illite, and has been depleted in phosphorus, titanium, and nickel. At Greymouth Coalfield, only moderate leaching effects are noted in the main coal bearing interval, the Rewanui Member, whereas in correlative coal measures at Pike River Coalfield some seams have been sufficiently leached to form boehmite.

(b) Brunner Coals Brunner coals generally are characterised by features attributed to slow accumulation in an extremely stable marginal marine environment. Within this context, substantial lateral variation in depositional setting has strongly influenced peat swamp character. At Greymouth, leaching of Brunner peats has resulted in an unusual, boehmite-rich mineral assemblage which is believed to have resulted from advanced decomposition of aluminosilicates and deposition of aluminium hydroxide, some of which may have been derived from outside the swamp. The principal factor controlling development of these unusual mineral characteristics may have been the extended life of the swamp, possibly more than 8 M.y. Survival of the swamp for such a long period without oxidation or major sediment incursion implies an ultra-stable environment, which is consistent with regional Paleocene geology (Nathan and others, 1986).

Very low ash Brunner coals are attributed to a combination of limited sediment supply and infrequent flooding, together with a variable degree of leaching depending on swamp character. At Pike River Coalfield, low ash coal has resulted from high water table swamps which were characterised by minimal leaching. Intermittent flooding has introduced little suspended sediment, but has allowed influx of rafted quartz grains which tend to dominate the aluminosilicate mineral matter.

At Buller Coalfield, Brunner coals result from peats which accumulated in swamps of widely differing character. Evidence from the Webb/Baynes area indicates that peat occurred in ombrotrophic, high-moor bogs where a combination of minimal sediment input and persistent leaching has reduced the inorganic matter to almost negligible values. Ultra-low ash values in "high-moor coal", and abundant boehmite in adjacent high ash "lagoonal coal", suggest transport of aluminium in solution as a result of low pH conditions, followed by precipitation in the less acid drainage areas.

Coals from the relatively large area of the Upper Waimangaroa Sector (Buller Coalfield) represent a variety of depositional environments, ranging from leached, boehmite-bearing raised bogs to low-moor peats which were contaminated by both muddy stream sediments and rafted material.

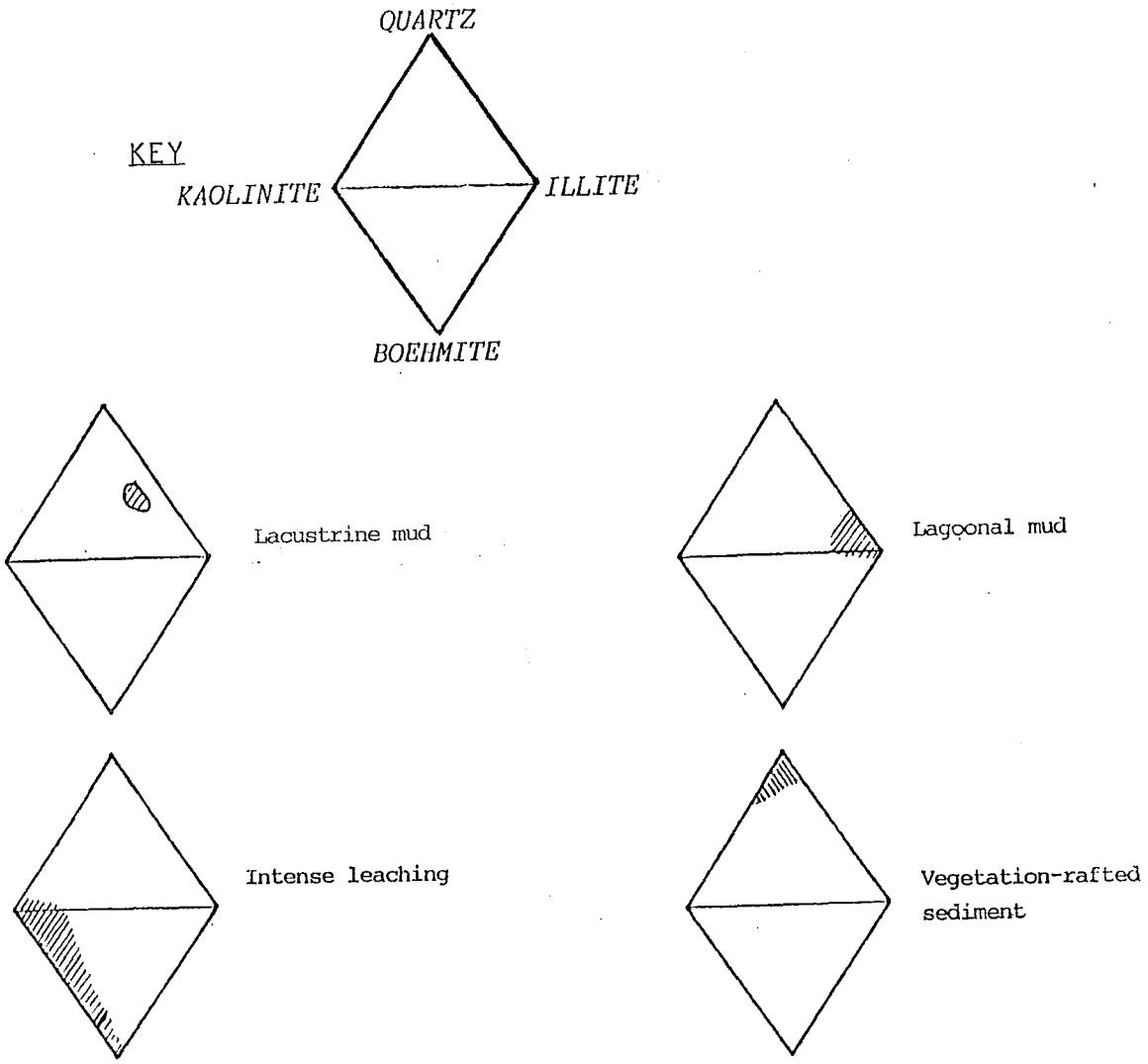


Figure 8.1 Summary of trends for aluminosilicate mineral matter, showing hypothetical fields for "end member" extremes.

Calculation of mineral assemblages for bituminous West Coast coals from their ash constituent analyses, using formulae based on observed mineralogy, provides a useful means of examining mineral trends within and between deposits. A summary of "end member" influences on alumino-silicate mineralogy is shown in Figure 8.1.

Sulphide minerals in Brunner coal originate chiefly from post-depositional sulphur enrichment, although some extremely pyritic coal shows evidence of syndepositional marine influence. Brunner carbonate minerals, which are chiefly represented by dolomite, occur in both syngenetic and epigenetic form. The origin of abundant carbonate mineralisation in the Pike River Brunner seam remains obscure, but is probably related to influx of calcium and magnesium, in solution, from seawater at the end of peat accumulation.

West Coast subbituminous coals contain chiefly organically bound mineral matter, except where sedimentary contamination is high. However, coals from the Rotokohu Coal Measures, together with some subbituminous coals of the Brunner Coal Measures, contain horizons of authigenic quartz which is probably of early diagenetic origin.

8.2 CONCLUSIONS

8.2.1 The Influence of Swamp Character on Mineral Matter

Throughout this work, interpretation of swamp character has relied in part on support from available maceral petrography and basin studies. There are too few geochemical and mineralogical studies of modern swamp analogues for the West Coast coals to permit completely independent assessment of coal-forming environments based on mineral matter alone. However, mineral matter studies can be regarded as a useful adjunct to other techniques of paleoenvironmental interpretation, and in some instances have allowed refinement of depositional models for West Coast coals.

Without further testing, it may not be possible to directly apply mineral matter-paleoenvironmental relationships observed in this study to coals in other areas, particularly in the case of Paleozoic coals overseas, which are dominantly subhydrous and inert-rich in comparison to West Coast coals. The lack of documented examples of overseas coals with hyperaluminous mineral matter suggests that some West Coast coals may be highly unusual.

Even within the range of West Coast coals, it is not possible to offer a "unified theory" for the influence of swamp character on aluminosilicate mineral matter, because swamp type and sedimentary regime were highly variable.

Although "high water table" swamps inferred for both Paparoa coals and Brunner coals have some common characteristics, such as limited kaolinite development and the presence of rafted quartz grains, there is no Brunner equivalent of a "low water table" Paparoa swamp, in view of

the invariably sparse inertinite content in Brunner coals. The "relatively oxygenated" Brunner swamps envisaged by Newman (1985a) are considered to be influenced by oxygenated water rather than direct aeration. Development of highly aluminous mineral matter in Paparoa and Brunner coals can, in each case, be attributed to well drained swamps which were raised above the regional water table. However, the Paparoa examples result from intermittent lowering of the regional water table and degradation of both peat and mineral matter, whereas the Brunner swamps appear to have been stable, ombrotrophic bogs.

8.2.3 Origin of Mineral Matter

(a) Kaolinite The high degree of crystallinity exhibited by kaolinite in the coals could result from either authigenesis or recrystallisation. It is not possible to clearly distinguish or estimate the proportion of kaolinite which is neoformed, i.e., formed from dissolved and transported components, except to a limited extent by microscopy.

A large proportion of neoformed kaolinite can be expected in coals where mobility of aluminium is indicated, within and near boehmite-bearing zones. Diagenetic reaction between aluminium hydroxide and free silica to form kaolinite is widely recognised (e.g., Millot, 1970; Weaver and Pollard, 1973; Velde, 1985), and probably accounts for the observed mutually exclusive occurrence of boehmite and quartz in some coals and carbargillites.

(b) Boehmite Although the only aluminium hydroxide mineral observed in the coals is boehmite, there is no clear evidence to show that this mineral was originally deposited in the peat. Initially, the "free" aluminium may have been present as adsorped Al^{3+}, amorphous hydroxide, or one of the crystalline hydroxide minerals.

On the basis of thermodynamic calculations, Chesworth (1972) showed that gibbsite (γ-$Al[OH]_3$) is the stable hydroxide species under earth-surface conditions, in the presence of solutions of low ionic strength. However, these data were obtained from purely inorganic systems, and may not be applicable to the natural environment. De Lapparent (1935) believed that humic acid solutions promoted the formation of boehmite in

preference to other hydroxide forms, and subsequent authors have made similar observations. Valeton (1972) considers that boehmite formation is favoured by reducing environments, and has drawn attention to a number of boehmite deposits which were formed in association with organic matter, under surface conditions.

In view of the above evidence, it appears that boehmite in coal probably developed as a syngenetic mineral. However, proof of this origin is difficult to establish. If gibbsite had formed, temperatures achieved during subsequent coalification to bituminous rank (Suggate, 1974) would have been sufficient to form boehmite by dehydration (e.g., Kennedy, 1959). Initial retention of aluminium in amorphous or ionic form must also be considered as a potential precursor of boehmite. Many lignites contain organically-associated aluminium (e.g., Kiss and King, 1979; Miller and Given, 1986), and in some cases exhibit hyperaluminous compositions (e.g., Black, 1982). No aluminium mineral other than kaolinite could be detected in the one hyperaluminous, subbituminous West Coast coal (B48).

Although the exact origin of boehmite in West Coast coals remains uncertain, it is clear that net accumulation of aluminium hydroxide, or its ionic equivalent, took place as a syngenetic process during peat accumulation. Existence of these deposits contradicts one principal conclusion of Lind and Hem (1975) regarding the significance of organic complexing, i.e.; "...one probably should not expect to find gibbsite accumulations in environments that were rich in accumulated organic debris, such as lake bottoms, swamps, or peat bogs".

(c) Illite and chlorite Throughout this work, illite in West Coast coals has been regarded as detrital. This concept is supported by evidence from microscopy and the pattern of illite distribution, but an authigenic origin for a proportion of the fine-grained illite cannot be discounted. The presence of illite in some coals where strong leaching of the peat is inferred implies that illite either survived the leaching episode, or has been formed subsequently.

It is difficult to establish the extent to which regrading of disordered illite, or illite-smectite, has taken place. The absence of organi-

cally-associated potassium in the coals could be attributed to adsorption by regrading clays. Whereas little systematic variation in illite character with inferred swamp environment or rank can be recognised, mineral matter in Paparoa seams shows a correlation between illite interlayering and sodium values. In view of the general leaching of alkalis from detrital minerals associated with these coals, the interlayering associated with high sodium values can be attributed to postdepositional pore fluid reactions.

The occurrence of chlorite in the coals is almost entirely restricted to hyperaluminous samples, indicating an authigenic origin related to an aluminium-rich environment. There are a number of routes by which chlorite could have developed in these coals. Aluminium-rich solutions are known to cause accumulation of gibbsite interlayers within smectite or degraded illite, leading to the development of a relatively acid-resistant, aluminous "soil chlorite" (Velde, 1985). Alternatively, chlorites can form in aluminium-rich environments independent of a dioctahedral aluminosilicate substrate, as demonstrated by records of chorite formation associated with bauxite deposits (Bardossy, 1959, cited Weaver and Pollard, 1967; Caillère et al., 1962; Swindale and Fan, 1967).

Formation of syngenetic or early diagenetic chlorite, by one or more of the mechanisms described above, may have taken place in the peat swamps when strong leaching ceased or declined. However, it is also possible that chlorite developed at various stages during coalification; Velde (1985) concludes that both 7A and 14A chlorites can be formed from temperatures from 50° upwards. All West Coast coals have achieved these temperatures (Suggate, 1974).

(d) Carbonates in Greymouth Brunner coal Fine-grained dolomite occurs in the Brunnerton coals in a form so well dispersed in the coal matrix that an excellent organic association for calcium and magnesium is maintained in all sink-float fractions (7.2.2 b). Dawsonite is also present in this coal, where it occurs in a fine-grained, well dispersed form similar to that of the dolomite, suggesting that these two carbonate minerals share a common origin. As far as can be determined, the occurrence of these minerals in disseminated form within coal has not been previously described.

Conditions controlling the formation of dawsonite in natural systems remain poorly understood, but are generally acknowledged to be characterised by a high partial pressure of CO_2, and solutions rich in ionic sodium and aluminate (Smith and Milton, 1966; Chesworth, 1971). Synthesis experiments by Chesworth (1971) indicated that very high pH (12+) was neccessary for dawsonite deposition, but records of natural occurrences suggest that less extreme conditions are required. The occurrence of dawsonite veinlets in Australian coal and coal measures has been discussed by Loughnan and Goldbery (1972), who consider that pH is not an important controlling factor, but reached no specific conclusions regarding the origin of dawsonite in coal. A prevalence of dawsonite in the seams in comparison to the enclosing sediments was tentatively attributed to locally high pCO_2, and the source of sodium and aluminium was considered to be aluminosilicate minerals outside the seams. A coexisting nordstrandite (a gibbsite/bayerite trimorph) was thought to be decomposed dawsonite.

The occurrence of dawsonite in Brunnerton coal differs from the Australian example in the following respects:

(i) Dawsonite is intimately dispersed in the coal, does not appear as veins, and is unknown outside the seam.

(ii) Abundance of dawsonite is extremely low; sodium values are not atypical of bituminous coals.

(iii) The coal seam contains abundant boehmite.

All the components necessary for formation of both dawsonite and dolomite could have been derived from the coal, in which sodium, calcium, and magnesium may have been initially present as adsorped cations. The time of carbonate formation is unknown, but the absence of nodular dolomite suggests that an early diagenetic origin is unlikely. During deep burial, thermal decarboxylation would have induced high pCO_2 conditions (Irwin et al., 1977), and development of alkali-rich pore fluid due to decomposition of carboxylate bonds (Renton, 1982). Elevation of pH by liberated alkalis would thereby provide a suitable environment for dolomite formation, and would increase the availability of aluminate ion, favouring dawsonite formation.

(e) Crandallite Although the origin of crandallite in West Coast coals remains obscure, the general pattern of occurrence suggests that concentrations of this mineral formed at or near the peat surface, in response to rare events when an abundance of phosphate was released in an environment containing a high concentration of Al^{3+}. Crandallite in the coals is dominantly calcian, in contrast to the rare earth equivalents normally found in soils and veins.

8.2.3 The Influence of Rank

Few mineralogical differences among West Coast coals can be attributed to variation in rank alone, except for the gross differences between bituminous and subbituminous coals. Whereas occurrences of boehmite and dawsonite are restricted to samples of Suggate rank 12 and above, no coals of lower rank are strongly hyperaluminous, therefore the the control of mineralogy by rank cannot be tested. Crandallite is limited to highly phosphatic samples, and ranges down to rank 10. Chlorite ranges from the highest ranks down to rank 10.5, dolomite to rank 9, and calcite to rank 8. Illite is common to all ranks, but shows no systematic variation in abundance, crystallinity or interlayering, at least within the rank range 10-14.

8.2.4 Comparison with Overseas Coals

When comparing West Coast mineral matter on a world-wide basis, it is necessary to emphasise the unusual character of the host coals, which are extremely low-ash and vitrinite-rich in comparison to most overseas coals. Mineral matter in West Coast coals may be unique with respect to the occurrence of the minor minerals; crandallite, boehmite, dawsonite, and chlorite can all be attributed to a highly aluminous environment, created by well drained, oligotrophic peat swamps in a variety of depositional settings.

Methods of statistical analysis employed for characterising mineral matter in overseas coals may not be applicable to the West Coast samples. Interpretations based on -2μ kaolinite-illite-expandable clay variation (Ward, 1977) may be misleading, in view of the substantial variation in abundance and character of illite, and the occurrence of

authigenic boehmite, dawsonite, and chlorite in the coals. However, results for three run-of-mine samples, processed by Ward's (1977) method have been plotted on a kaolinite-illite-expandables diagram (Figure 8.2). The low abundance of expandables noted from whole LTA is also present in the -2μ fraction. In comparison to coals of the Springfield-Harrisburg Coal Member, Illinois Basin (Ward, 1977), and most Australian coals (Ward, 1978), the West Coast samples are kaolinite-rich.

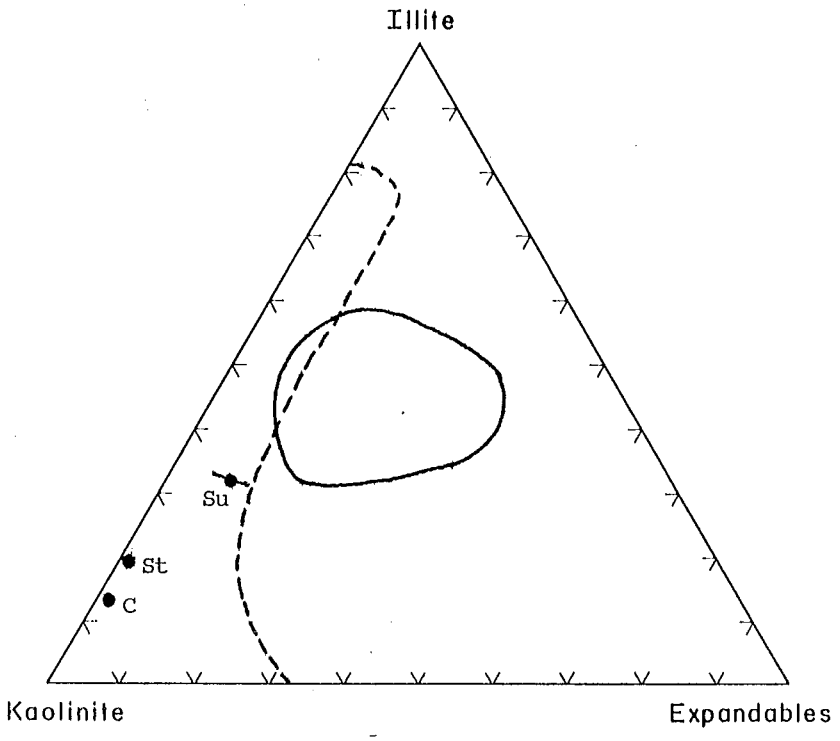


Figure 8.2 Mineralogy of -2μm fraction of mineral matter for 3 run-of-mine West Coast coals. The solid line encloses the points plotted by Ward (1977) for Springfield-Harrisburg coals, Illinois Basin. The dashed line indicates the limit expected for most West Coast coals, as estimated from the mineralogy of whole LTA.

Su: Sullivan Mine (Brunner coal, Buller Coalfield)
Bar indicates uncertainty in expandables measurement

C: Charming Creek Mine (Brunner coal, Buller Coalfield)

St: Strongman Mine (Paparoa coal, Greymouth Coalfield)

8.3 APPLICATIONS

8.3.1 Coal Characterisation: Relevance to Future Work

It is hoped that this work will provide a useful base of information from which future studies of mineral matter in West Coast coals can proceed. The results of this project should also be relevant to future studies of coalfield paleoenvironment, coal utilisation, environmental protection, and general interpretation of analytical data for West Coast coals. Interpretations of trace element data, in particular, may be misleading unless mineralogical variation is examined. For example, the widespread but erratic occurrence of crandallite in the coals can be expected to have a major effect on the distribution of strontium, barium, and various heavy metals and rare earths which commonly occur in this mineral (Palache et al., 1960; Norrish, 1968).

8.3.2 Paleoenvironmental interpretation

As outlined above, many of the observed relationships between mineral matter and paleoenvironmental indicators are of value in reconstructing depositional settings and peat swamp character. One of the more direct applications of mineral matter studies is the distinction of detrital minerals from authigenic minerals, to reveal the true pattern of clastic sedimentation, as demonstrated by the following example.

Exploration of the Brunner seam at Pike River Coalfield initially proceeded by mapping and extensive channel sampling of outcrop coal on the exposed western side of the field. Later, six drillholes intersected the seam down-dip from outcrop. The results of proximate analyses showed whole seam ash values for the drillholes to be generally greater than for the outcrop areas.

Subsequent petrological and geochemical analyses showed that all the drillhole samples contain abundant dolomite, often accompanied by calcite. These carbonate minerals have been almost completely leached from outcrop coal by weathering. Surprisingly, gypsum is not prominent in outcrop samples, probably because of the high rainfall and good drainage of the steeply sloping areas.

The pattern of contoured dry basis ash values for the coalfield (Figure 8.3) conflicts with a coal type-lithostratigraphy based paleoenvironmental reconstruction for the Brunner seam (Newman, 1985a), which predicts relatively high ash in areas believed to have been near the swamp margin. Very high ash zones in the south and southwest are attributed to the influence of barrier bar and lagoonal sedimentation. In the central portion of the coalfield, sampled by drilling, a particularly low ash zone is predicted, but the true pattern of detrital mineral matter content is obscured by the abundant authigenic carbonate minerals, which appear to have no relationship to detrital sedimentation.

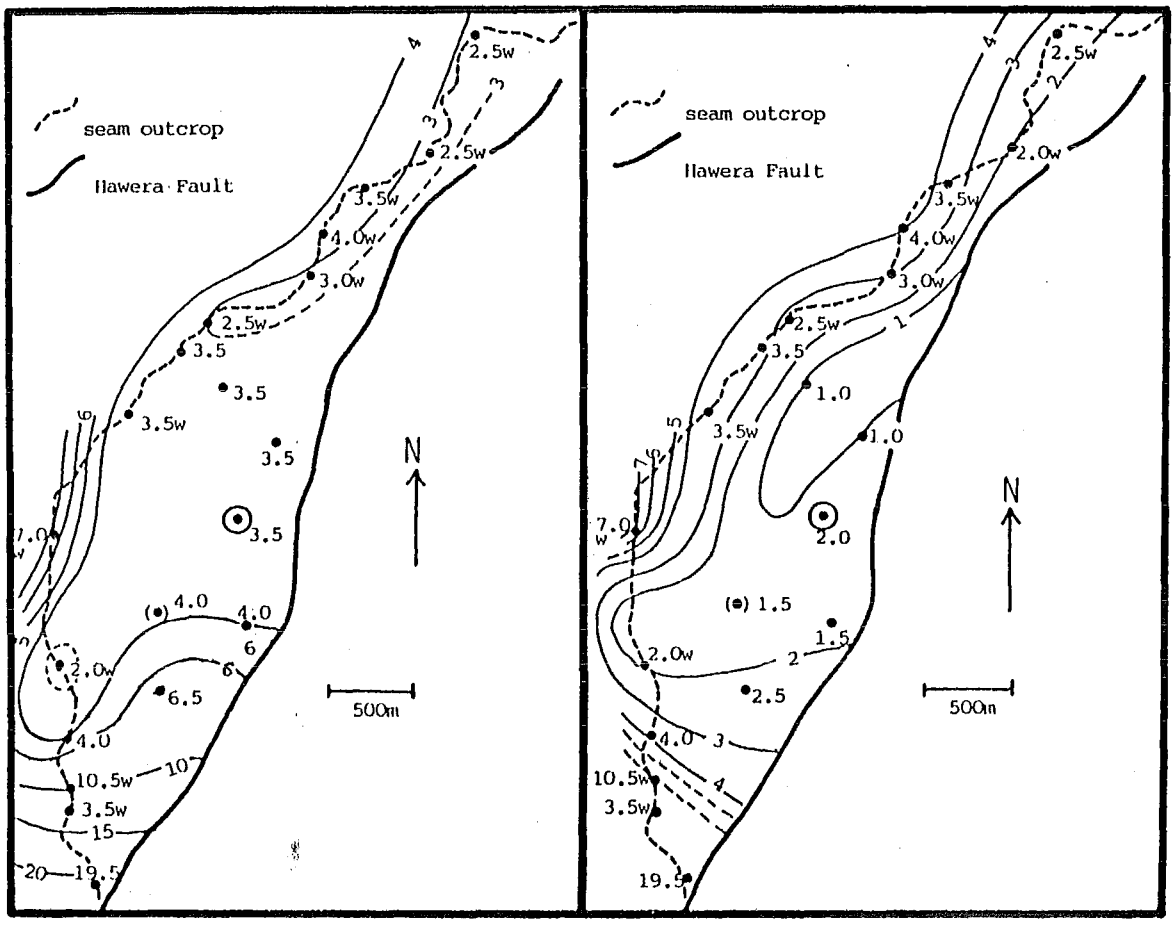


Figure 8.3(left). Contoured ash (dry basis) values for Brunner seam, Pike River Coalfield.

(right). Contoured ash values as above, using derived values for 'detrital ash', removing the effect of authigenic carbonate.

Note: Data point in brackets adjusted for probable seam repetition by faulting, and data point circled adjusted for high ash seam floor material included in bottom composite by error.

Analysis of drillhole samples for ash constituents, together with a knowledge of the range of minerals present in the coal, permits recalculation of ash values to omit the carbonate contribution. This recalculation has been achieved by simple elimination of CaO, MgO, and SO_3 from ash values for each sample. Fe_2O_3 has not been eliminated, because ash constituents have not been analysed for all the outcrop samples, and unlike the carbonate minerals, weathering has removed only a small proportion of pyrite from outcrop coal. Much of the iron in severely weathered coal is retained as hematite and other oxides. The distortion in recalculated ash values due to neglecting Fe_2O_3 is considered to be very small.

Contours for 'detrital ash', obtained by the recalculation process (Figure 8.3), suffer from the limited number of data points, but the general pattern which emerges is consistent with the paleoenvironmental model proposed by Newman (1985a) on the basis of seam geometry, coal petrography, and volatile matter variations, and may have value in predicting seam continuity and coal characteristics between and beyond the drillholes.*

8.3.3 Expression of Analytical Parameters to a Mineral Matter Free Basis

(a) Mineral matter/ash ratios. Proper assessment of the properties of organic matter in coal requires recalculation of analytical results to a dry, mineral matter-free basis. Suggate (1959) has shown that nitrogen and sulphur should also be eliminated by calculation.

Conventional methods of achieving these corrections are commonly based on assumptions concerning mineral composition, or indirect methods used to determine the "average" influence of mineral matter. These fixed formulae methods have been reviewed by Watt (1968), Scholz (1980), Gluskoter et al. (1981), and Ward (1984, 1986). A formula for New

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* It should be noted that, due to an error during compilation, the relevant section of Newman (1985a) illustrates uncorrected ash values in Figure 112, instead of 'detrital ash' values as stated in the caption.

Zealand coals was originally derived by Suggate (1959), who applied an average mineral matter/ash value of 1.1 to all coals. More recently, Gray (1980, 1983a) used linear regressions of analytical parameters (specific energy, volatile matter, and organic elements) against ash to derive mineral matter/ash values for individual coal regions. This technique, which was developed by Brinsmaid (1909), simply provides a more accurate value for "average" mineral matter, and cannot compensate for the fluctuations exhibited by individual samples.

An alternative approach to the problem of correction factors is direct measurement of actual mineral matter, by either dissolving the minerals in acids or oxidising the organic matter, commonly by RF plasma ashing. These techniques are largely successful, but very time-consuming (Watt, 1968; Miller et al., 1979; Gluskoter et al., 1981; Ward, 1984, 1986).

Estimation of mineral matter by calculation of the mineral assemblage ("normative analysis") has been succesfully demonstrated by Pollack (1979). A similar procedure, modified to include minor minerals and to adjust to major mineralogical variations, has been used in this work to derive the mineral matter/ash factors listed in Appendix 2. These factors may be compared with the fixed value of 1.07, derived by the method of Gray (1980), and used by CRA for all West Coast coals. The wide fluctuation of factors in Appendix 2 suggests that the use of any fixed formula may incur substantial errors.

(b) Correction of volatile matter values. Mineral matter-free correction of volatile matter measurements requires an accurate assessment of both mineral matter/ash ratios and volatiles of mineral origin, i.e., CO_2, and water of hydration.

Suggate (1959) has shown substantial variation in volatile matter values between serial (isorank) samples of West Coast coals, thereby demonstrating a wide variation in coal type. As a result of more recent work this type variation is considered to be a result of variation in character of the dominant maceral, vitrinite, as opposed to a simple variation in maceral proportions. Studies by Newman & Newman (1982), and Newman (1985a) show a well defined inverse correlation between

volatile matter (VM) and mean, maximum vitrinite reflectance ($\bar{R}_o$). This relationship is linear for suites of Brunner coals of broadly similar rank, and the slope of VM/$\bar{R}_o$ declines with decreasing rank (Figure 8.4). The degree of scatter for plotted data points for specific suites of coals is successively reduced if volatile matter values are recalculated using corrections for mineral matter and sulphur. Vitrinite reflectance therefore appears to offer an independant means of comparing the applicability of various volatile matter correction methods (N.A. Newman, 1985).

The results of several different correction methods used for data from three West Coast coal deposits were obtained and compared by the use of simple BASIC programs run on a microcomputer (Table 8.1). The linear regression of calculated volatile matter against reflectance was carried out by the least squares method, providing values for slope (%VM/%$\bar{R}_o$) and a projected intercept at $\bar{R}_o$=0. The intercept is theoretical, lying well beyond the linear portion of the plot. A 'goodness of fit' is shown by r^2, the square of the correlation coefficient. Sigma represents the standard deviation for the calculated volatile matter values with respect to the regression line, i.e.,

$$\frac{(VM_{regr.} - VM_{calc.})}{N - 2}$$

The seven different volatile matter versions, designated V1 to V7 in Table 8.1, represent three groups, as follows.

(i) V1 is obtained by conventional dry, ash free calculations.

(ii) V2, V3, and V4 are based on the simple Parr-type formula used by Suggate (1959) to correct volatile matter for all New Zealand coals, i.e.,

$$VM_{dmmsf} = \frac{100(VM - 0.1A - S)}{100 - 1.1A - S} \quad \text{(all on a dry basis)}$$

This calculation, which is used for all the V3 values, corrects to a sulphur-free basis, and assumes that all the sulphur enters the volatile matter. Reflectance-volatile matter graphs prepared from data for Buller coals (Newman 1985a, 1985b) show that the Suggate formula substantially over-corrects sulphur-rich samples. A better plot was obtained by omitting the sulphur terms (as in V2), and a

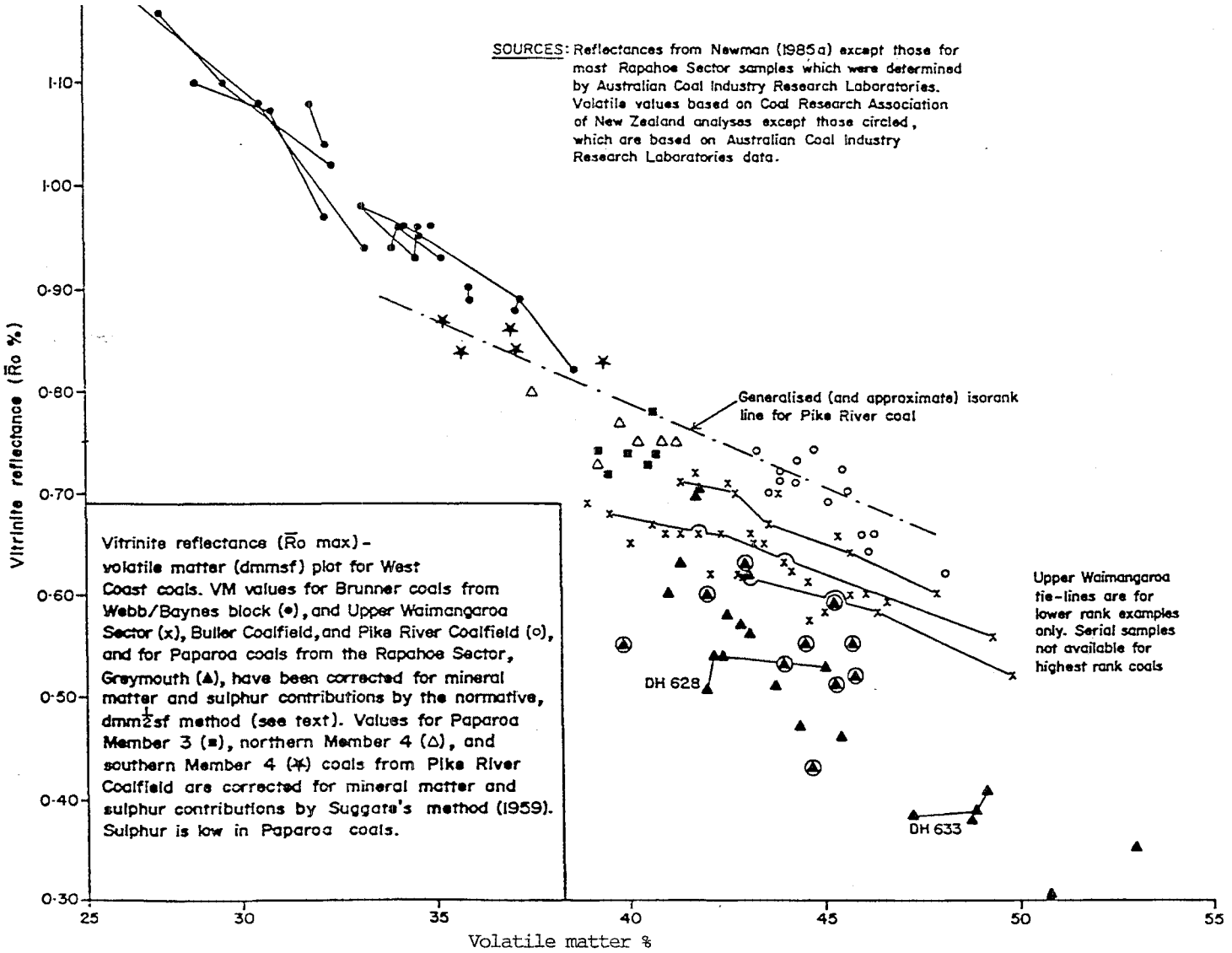

Figure 8.4 Vitrinite reflectance/volatile matter plot for coals sampled during recent West Coast exploration programmes. Tie-lines link isorank serial samples. From Newman (1986).

further improvement resulted from a modified 'sulphur free' version (V4) in which the numerator contains the term 1/2S to represent the partitioning of sulphur between volatile matter and coke or char during pyrolysis. The assumed partitioning factor of 1/2S has recently been confirmed by sulphur analyses (V.R. Gray, pers. comm.).

(iii) V5, V6, and V7 are calculated by means of 'normative mineral analysis' procedures, whereby ash constituents are partitioned among different minerals according to known mineral matter data. This permits water of hydration and CO_2 to be subtracted from the volatile matter, and appropriate corrections made to the mineral matter/ash ratio. Three versions have been formulated, each differing in their treatment of the sulphur correction.

V5 is expressed dry, mineral matter free (dmmf), and has no correction for sulphur except pyritic sulphur, half of which is assumed to be evolved during pyrolysis:

$FeS_2 + H_2 \longrightarrow FeS + H_2S$

The general form of the volatile matter correction formula applied is as follows:

$$VMdmmxSf = \frac{100(VM - \Sigma h - \Sigma c - 1/2Spy - xS)}{100 - A - \Sigma h - \Sigma c - S + SO_3(a) + \Sigma f}$$

(all dry basis)

Where xS represents the fraction of organic sulphur (dry basis) to be eliminated;

VM is volatile matter;

Σh is the sum of water of mineral hydration;

Σc is the sum of mineral CO_2 evolved;

S is total sulphur;

$SO_3(a)$ is sulphate in ash;

Spy is pyritic sulphur;

Σf is the sum of factors required to compensate for oxidation of different iron minerals to leave Fe_2O_3 in ash.

Any proportion of organic sulphur can be eliminated. If x = 0 is selected (dmmf), sulphur is not distinguished from the coal substance, and the term -S in the denominator is replaced by -S(py). The method assumes that sulphate in coal is negligible. Forms of sulphur have been

determined for only a few West Coast coals, but pyritic sulphur can be readily calculated for Brunner samples from their iron content. The assumption that all iron exists as sulphide in unweathered coals appears valid for all except very high ash samples.

The Pike River Brunner samples, which contain a highly variable assemblage of sulphide, carbonates, silicates, and quartz, respond well to the normative analysis approach to volatile matter correction, and demonstrate the unsuitability of the simple Suggate formula for such coals. The regressions based on drillhole samples alone show the 1/2S modification to be the best of the Suggate formula versions. If outcrop samples are included, the dmmf version yields best r^2, probably because of severe weathering effects. For both populations, the 1/2S and sulphur-free versions of the normative analysis correction give the best results among the eight regressions. A further improvement can be made if the outcrop samples are adjusted for weathering, which can be estimated from moisture values (Newman, 1985a, 1986).

	REGRESSION	SLOPE	INTERCEPT	r^2	SIGMA
	Pike River Brunner coal, drillcore only : 14 samples VM=43-48% (V6)				
V1	VM daf	-30.284	67.606	0.558	1.048
V2	Suggate dmmf	-29.474	66.797	0.564	1.008
V3	Suggate dmmSf	-12.928	53.834	0.275	0.816
V4	Suggate dmm½Sf	-29.161	66.501	0.566	0.993
V5	normative dmmf	-28.342	64.817	0.688	0.741
V6	normative dmm½Sf	-27.598	64.183	0.687	0.723
V7	normative dmmSf	-11.658	51.731	0.211	0.875
	Pike River Brunner coal, drillcore and outcrop: 18 samples VM=43-48% (V6)				
V1	VM daf	-22.929	62.185	0.370	1.287
V2	Suggate dmmf	-22.098	61.326	0.332	1.347
V3	Suggate dmmSf	-8.835	50.704	0.068	1.403
V4	Suggate dmm½Sf	-21.795	61.025	0.317	1.377
V5	normative dmmf	-24.840	62.819	0.590	0.891
V6	normative dmm½Sf	-24.354	61.732	0.573	0.903
V7	normative dmmSf	-11.606	51.569	0.166	1.117
	Webb/Baynes Brunner coal, Buller Coalfield: 24 samples VM=26-38% (V6)				
V1	VM daf	-30.516	64.176	0.913	0.926
V2	Suggate dmmf	-29.615	63.023	0.943	0.717
V3	Suggate dmmSf	-30.962	62.644	0.914	0.934
V4	Suggate dmm½Sf	-30.618	63.597	0.951	0.679
V5	normative dmmf	-29.468	62.748	0.948	0.675
V6	normative dmm½sf	-30.253	63.142	0.955	0.647
V7	normative dmmSf	-30.258	61.973	0.918	0.888
	Rapahoe Sector Paparoa coal, Greymouth Coalfield: 25 samples VM=41-48% (V6)				
V1	VM daf	-13.097	51.448	0.313	1.522
V2	Suggate dmmf	-12.948	51.115	0.305	1.535
V3	Suggate dmmSf	-12.716	50.706	0.301	1.521
V4	Suggate dmm½Sf	-12.977	51.101	0.304	1.541
V5	normative dmmf	-15.131	51.942	0.381	1.515
V6	normative dmm½sf	-15.172	51.932	0.380	1.522
V7	normative dmmSf	-14.914	51.538	0.374	1.515

Table 8.1 Values from calculated regression of different volatile matter versions against vitrinite reflectance (adapted from N A Newman (1985); Table 2).

For the Webb/Baynes samples from Buller Coalfield, the advantage of normative analysis correction is less clearly defined. The 1/2S, normative value is only a little better than the 1/2S Suggate version (r^2 0.955 and 0.951 for V4 and V6 respectively). There are several possible reasons for the limited success of the normative analysis corrections for these coals. Mineral variation is known to be inadequately assessed, partly due to the affects of weathering. There are insufficient data to permit correction refinements for iron oxides and sulphates, both of which are definitely present in some samples, particularly in topmost plies. The top ply from Drillhole 1241 (31/110) produces an especially large negative volatile matter deviation, and is known to contain a substantial amount of hematite and other iron oxides. Furthermore, no factor has been incorporated to correct for the effect of weathering on the pyrolysis behaviour of the coal substance.

Data for 25 Paparoa coal samples of broadly similar rank from the Rapahoe Sector of Greymouth Coalfield were also available for regression analysis. All correlations obtained for these samples are inferior to the Brunner examples. Normative analysis provides substantially better results than do the other formulae, very similar results being obtained for V5 (r^2 0.381) and V6 (r^2 0.380). The small degree of difference between the various sulphur versions is due to the very low sulphur content of the samples.

Several shortcomings of the normative correction process can be identified for future refinement, i.e.,

(i) More detailed, actual mineral analysis may be required in situations where more than one mineral interpretation of ash constituents exists, e.g., some Buller composites contain both quartz and boehmite, which is interpreted by normative analysis as kaolinite.

(ii) The effects of weathering on the mineral assemblage have been neglected. The presence of sulphates will cause a substantial increase in the overall mineral hydration.

(iii) The reactions of certain minerals, or combinations of minerals in coal during pyrolysis remain poorly understood, and should be investigated. Such reactions include catalytic effects on the coal substance in addition to purely inorganic mineral transitions.

(iv) The proportion of non-mineral, or non-crystalline, organically

bound inorganic elements in bituminous coals is relatively small and has been neglected, but these components must be incorporated in mineral matter corrections for coals of lower rank.

8.3.4 Seam Correlation.

It is doubtful whether mineral matter characteristics will provide a reliable method of seam correlation for West Coast coals, in view of the rapid lateral variations shown by most seams. Seam correlation is rarely necessary in the Brunner Coal Measures, but where multiple seams occur (e.g., Reefton), distinction on the basis of phosphate values may be possible. Among Paparoa coals, seams in the Dunollie Member are distinctively pyritic and kaolinite-rich, but characterisation of any particular seam from the Morgan or Rewanui Members would be speculative if based on drillcore. Data for run-of-mine coals suggest that bulk sampling may allow characterisation of the seams over limited areas. TiO_2/Al_2O_3 ratios may be most useful for distinglushing seams in the Rewanui Member.

8.3.5 Implications for industrial utilisation

(a) Combustion. Most West Coast mines supply coal for domestic and industrial heating. Small-scale combustion, commonly in low-intensity furnaces, gives rise to few problems. However, low ash fusion temperatures for many of these coals may be a serious limitation to their use in large-scale installations. The common abundance of iron-bearing minerals in both Paparoa and Brunner coals strongly depresses ash fusion temperatures (Hughson, 1953), particularly where high calcium values are also present. Upgrading is possible by washing, but Hughson (1953) has noted that the extent of beneficiation required to improve ash fusion temperatures for Paparoa coals is not practical. Sink-float data for some Brunner coals suggest that coal washing on a commercial scale will increase the iron content in ash, due to the occurrence of uniformly distributed, fine grained pyrite. However, some extremely high ash fusion temperatures are also exhibited by coals which are kaolinite-rich or hyperaluminous.

The sodium-rich coal from Heaphy Mine might be expected to cause fouling in boilers, but no problems have been reported in this respect. A large proportion of the output from this mine is sold for domestic use, where the high alkali content is mildly beneficial in retaining sulphur in ash (Newman, 1987a).

(b) Manufacture of metallurgical coke. The high-swelling, reactive-rich coals found in the West Coast region are valuable blend components for the production of metallurgical coke. Much of the output from Buller Coalfield is currently exported for this purpose. The constraints imposed by inorganic matter in these coals are reduced by the generally low mineral matter content.

For specialised metallurgical purposes, some care may be required to avoid occasional high concentrations of titanium and phosphorus. Aluminium anode carbon production requires stringent control of impurities; although limited areas of Buller coal meet these specifications (Marshall, 1983), a coal-cleaning plant would be required to sustain a large-scale industry. Sink-float data suggest that coal washing would increase the aluminium content of most coals, but some undesirable elements, such as phosphorus and sodium, may also increase.

(c) Cement manufacture. Ideally, a cement industry can utilise high ash coal which is unsuitable for other purposes, although at present, such operations would not be economic. However, for future use, suitable high ash deposits can be delineated at Greymouth and Pike River Coalfields. Very large deposits of high ash coals in the barren belts of the Buller Coalfield are probably unsuitable for cement making, due to the presence of boehmite (Newman, 1987c). The use of highly aluminous feedstock for cement making results in an excess of calcium aluminate in the clinker, which adversely affects setting properties.

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APPENDIX 1

LOW TEMPERATURE ASHING PROCEDURE

Low temperature oxidation of coal samples was carried out in a LFE Corporation RF asher, model LTA 304(2). This machine has two chambers of 4 inches diameter. General recommendations for low temperature asher operation are provided by Miller et al. (1979), who stress the importance of controlled oxidation conditions. In particular, they point out increased loss of sulphide and retention of sulphur as sulphate if oxidation is prolonged at low temperatures. Ideal oxidation temperatures are not usually quoted by workers using the LTA technique, partly because of measurement difficulties. However, 150°C is generally accepted as a safe maximum which will not cause excessive mineral decomposition (e.g., Ward, 1978). Because of variations in design and construction of low temperature oxidation apparatus, it is considered unwise to adopt published settings of power level, oxygen flow etc. Temperature measurement cannot be carried out by placing metallic devices within the chambers, and is therefore restricted to observation of mineralogical transformations or optical measurement techniques.

Several workers have estimated oxidation temperatures by scanning the sample with an infra-red optical thermometer via the glass chamber lid (e.g., R. Soong pers. comm.). Because of the low transmittance of pyrex glass over the wavelengths usually employed by these thermometers, results from the method may be unreliable. Experiments carried out by the writer, using a model IT-4 Thermal Master infra-red thermometer (bandwidth approx. 9.5 - 11.5 μm), show that indicated temperatures are largely controlled by the surface temperature of the pyrex chamber. A temporary chamber lid was constructed whereby a small aperture was sealed with a polished alkali halide window, cemented in place. This provided a good response to calibration surfaces, which were coated with powdered coal to eliminate errors arising from different emissivities.

Test runs under fixed-power conditions showed that coal surface temperatures would initially rise when small flow rates of oxygen were introduced to the chamber, but the temperatures decreased and stabilised as the flow rate was increased. This behaviour is assumed to be due to heat removal by surplus oxygen flow (Figure A1.1). A flow rate of 250 ml/minute (to 2 chambers) was found to provide good oxidation rates and acceptable economy of oxygen consumption. A test run at this flow rate indicated a linear relationship between RF power setting and coal surface temperature, as shown in Figure A1.2. Spot measurements of fixed settings showed some variation of this relationship, possibly as a result of different sample characteristics and a change in ambient temperature of the apparatus after several hours operation. Settings of 90 watts total power, and 250 ml/minute oxygen flow, were selected as standard conditions, under which maximum oxidation temperatures were estimated to be 140°C.

Samples were stirred each 3 - 4 hours, except in the case of very low ash coals, for which stirring was unneccessary because of the low yield of mineral matter. Oxidation of high sulphur samples caused crystallisation of sulphuric acid hydrates on the chamber lid, and condensation of sulphuric acid on the chamber walls, and probably within the samples themselves, which were difficult to oxidise to completion. Additional problems were caused by natural sulphates (weathered or oxidised samples) and synthetic sulphates (low rank coals), which impeded the oxidation process, probably by coating the organic matter.

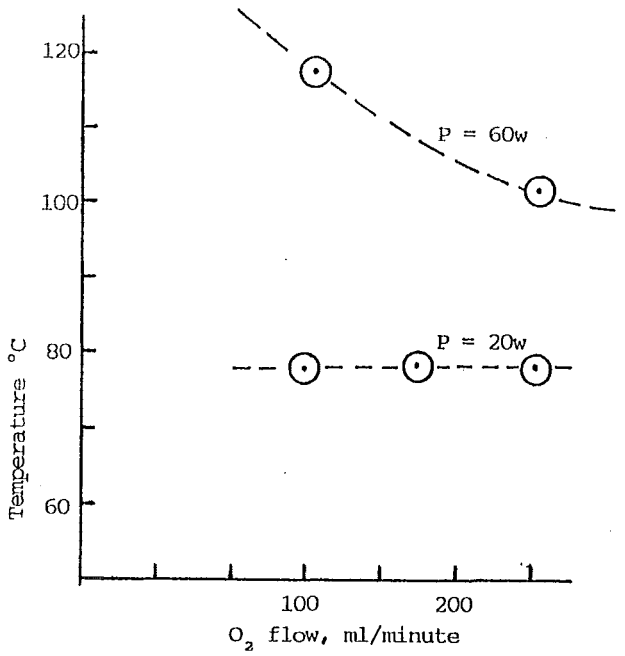

Figure A1.1 Isopower surface temperature of powdered coal at different oxygen flow rates. Data refer to two chambers in parallel.

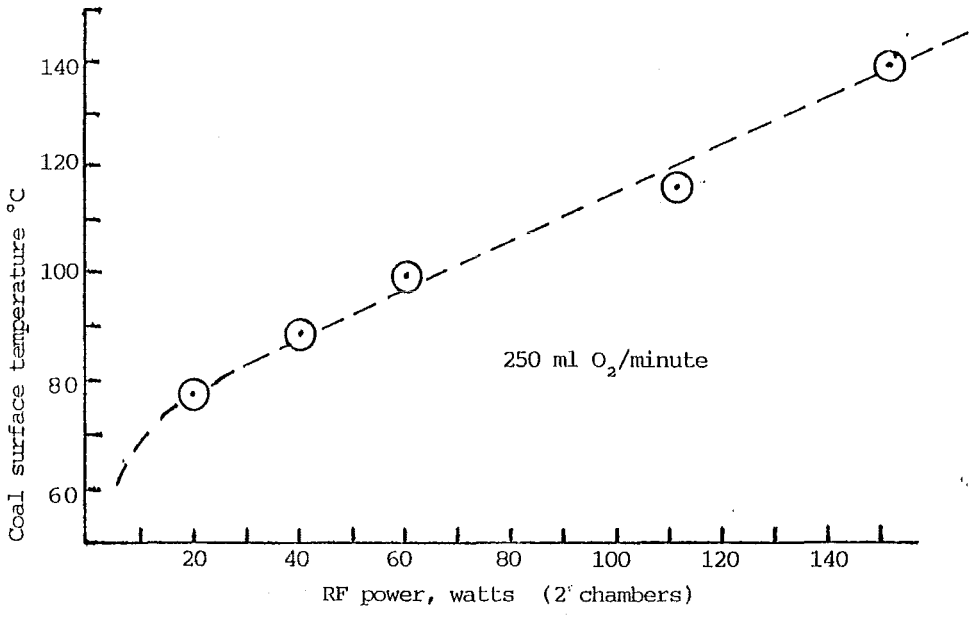

Figure A1.2 Isoflow surface temperature of powdered coal at different RF power settings. Data for 2 chambers in parallel.

APPENDIX 2

Ash constituents analyses and calculated mineral assemblages for West Coast coals.

Sample	Ash ad	MgO	Na2O	SiO2	Al2O3	SO3	P2O5	Fe2O3	MnO	TiO2	CaO	K2O	Sr(ppm)	Ni(ppm)
P3	2.9	0.28	1.25	68.71	25.35	0.00	0.65	1.60	0.01	3.03	0.78	0.45	1387	219
P4	2.1	0.44	1.91	47.32	35.41	0.02	1.01	4.01	0.00	6.15	1.22	0.47	1131	324
P8	18.4	0.68	0.33	68.36	22.29	0.00	0.34	1.18	0.01	2.93	0.18	2.57	455	136
P9	11.4	0.30	0.41	70.39	20.70	0.00	0.82	1.13	0.00	3.29	0.45	0.86	1079	309
P10	6.1	0.97	0.73	50.06	33.73	0.00	4.55	2.81	0.06	1.05	2.90	4.39	5302	324
P11	2.4	3.76	3.78	28.14	21.34	3.79	0.41	30.04	0.07	2.60	5.35	0.78	507	156
P12	2.3	2.17	3.39	52.98	20.28	2.31	0.86	8.03	0.02	1.17	4.27	1.54	557	447
P13	3.8	0.23	1.07	50.04	28.07	0.51	6.21	1.09	0.00	8.34	2.65	0.26	11137	167
P14	1.6	0.99	5.31	49.12	25.56	0.75	0.13	8.94	0.04	1.29	2.67	1.44	417	636
P15	12.4	1.44	0.14	6.02	2.39	0.53	0.83	85.99	0.59	0.12	1.31	0.21	n.d.	n.d.
P16	0.9	3.09	1.28	32.86	20.20	4.17	0.10	33.68	0.29	0.53	3.51	0.19	86	249
P17	1.6	4.41	1.19	33.75	11.61	1.74	0.11	40.90	0.34	0.51	2.95	0.15	15	82
P18	2.0	1.07	2.43	46.26	29.37	1.14	0.09	17.92	0.17	0.60	1.19	0.18	113	214
P19	45.5	0.97	0.29	73.25	13.41	0.18	1.24	6.71	0.08	0.84	0.78	3.13	2212	35
P20	6.4	0.13	0.36	85.81	9.20	0.22	0.17	0.36	0.00	1.31	0.17	0.30	281	604
P21	13.5	1.09	0.00	50.08	39.76	0.00	3.02	1.95	0.03	1.39	1.36	3.73	985	184
P23	11.3	3.31	0.42	9.22	4.98	0.53	0.15	76.01	0.58	0.26	1.11	0.33	0	<10
P28	13.0	0.30	0.32	69.07	19.51	0.21	1.91	0.86	0.00	5.55	1.06	0.26	4868	238
P30	3.6	1.26	0.11	26.06	20.75	1.16	0.13	47.46	0.71	0.66	1.41	0.32	341	458
" S1.5	51.2	1.66	0.00	18.91	13.83	1.40	0.09	57.91	1.04	0.15	1.19	0.35	n.d.	n.d.
" F1.5-S1.3	1.5	0.84	0.40	37.21	33.39	0.10	0.31	20.26	0.12	1.04	1.98	0.36	"	"
" F1.3	0.8	0.96	1.35	34.39	31.44	3.50	0.26	17.01	0.09	2.84	4.94	0.30	"	"
P31	5.8	0.54	0.42	55.50	25.95	1.60	0.63	9.17	0.19	1.64	2.80	2.00	1368	242
P32	27.3	0.47	0.23	60.71	23.73	0.43	0.08	11.24	0.06	1.55	0.82	1.58	364	43
26/130	29.2	0.59	0.37	63.00	25.36	0.31	0.09	3.69	0.00	1.97	0.23	1.89	176	75
26/132	30.1	0.98	0.36	66.52	23.86	0.03	0.05	3.81	0.00	1.18	0.17	3.29	42	86
21/922*	7.7	1.10	0.57	51.80	24.20	0.84	0.44	7.50	0.02	2.30	2.70	2.60	n.d.	n.d.
27/156	6.1	0.97	0.41	50.21	23.87	1.47	4.33	4.34	0.00	2.92	7.75	2.23	1505	110
27/496	5.9	1.38	0.64	51.32	25.76	0.49	1.93	9.36	0.06	2.42	3.46	2.96	1244	142
30/337	6.7	0.87	0.44	55.20	27.18	0.18	3.56	3.32	0.00	2.61	2.81	2.78	1336	162
21/913*	5.1	2.20	0.58	52.40	18.50	2.20	0.44	12.20	0.07	0.92	4.50	2.40	n.d.	n.d.
27/487	3.6	3.85	0.63	47.76	20.37	5.15	1.28	9.10	0.04	0.85	7.53	2.73	2842	138
30/329	5.9	2.11	0.37	55.50	23.04	1.64	1.11	9.36	0.07	1.00	2.69	3.09	1331	230
37/016	2.9	2.85	0.51	51.25	16.22	2.76	0.45	18.32	0.15	0.96	2.90	1.69	n.d.	n.d.
" S1.5	53.2	3.95	0.00	41.41	13.80	1.68	0.45	29.61	0.24	0.46	3.53	2.04	"	"
" F1.5-S1.3	7.4	2.29	0.60	59.42	18.81	3.82	0.62	7.10	0.06	0.95	3.31	1.59	"	"
" F1.3	0.9	1.13	2.26	66.73	17.63	0.74	0.46	4.20	0.02	1.79	1.77	0.93	"	"

Table A2.1 Ash constituents analyses for Paparoa coals: field, run-of-mine, and miscellaneous samples.

GREYMOUTH COALFIELD

Sample	M%ad	A%ad	S%ad	MgO	Na2O	SiO2	Al2O3	SO3	P2O5	Fe2O3	MnO	TiO2	CaO	K2O	Sr(ppm)	Ni(ppm
P33	0.8	6.9	0.4	1.58	2.12	31.68	26.97	0.00	0.10	25.94	0.24	1.47	8.24	0.86	1350	184
P34	0.0	19.2	0.0	0.46	0.58	52.99	37.90	0.13	0.47	0.95	0.00	1.40	0.61	2.15	1207	120
P35	0.0	18.4	0.0	0.31	0.28	83.64	10.37	0.40	0.79	0.83	0.01	1.00	0.79	0.50	1902	101
P36	0.0	27.8	0.0	0.17	0.16	80.76	11.98	0.23	1.94	0.60	0.00	1.15	0.82	0.20	4242	74
27/534	2.4	10.1	0.4	1.22	0.06	62.52	25.50	0.45	0.48	2.68	0.01	1.35	0.77	4.11	1037	182
27/535	2.2	4.2	0.8	0.83	0.21	53.34	21.91	2.10	0.90	13.53	0.02	1.28	2.86	1.25	3394	386
27/537	1.4	7.6	0.4	1.73	0.14	52.32	16.39	2.83	0.09	19.11	0.34	1.05	2.72	1.39	452	136
27/541	3.4	6.7	0.5	1.19	1.05	60.25	25.65	1.59	0.42	3.00	0.00	4.20	1.93	0.80	1351	268
27/543	2.0	15.1	0.2	0.65	0.02	71.43	17.13	0.54	0.42	1.40	0.00	5.81	0.85	0.82	837	208
27/544	6.6	6.9	0.3	1.14	0.06	58.32	25.85	1.28	0.82	4.82	0.02	3.49	2.01	1.41	1770	265
27/673	3.5	2.5	0.4	1.71	1.55	47.09	24.25	5.33	0.09	9.03	0.00	1.18	5.40	1.41	4798	360
27/707	2.2	7.3	0.3	0.82	2.89	53.40	27.43	1.68	1.84	3.11	0.02	5.88	2.72	0.55	2961	2224
27/708	2.9	3.7	0.5	1.73	2.79	52.07	23.91	3.46	0.30	6.38	0.07	2.04	3.50	0.89	3268	1006
27/713	1.8	5.2	0.5	0.55	0.33	69.09	22.19	0.24	0.66	1.16	0.01	2.92	0.50	1.50	2786	657
30/119	3.7	8.9	0.5	0.66	0.61	72.19	16.33	0.99	0.33	3.37	0.00	2.41	1.04	0.83	1943	272
30/122	2.2	5.7	0.5	0.43	0.00	47.09	38.99	0.66	2.46	4.91	0.05	2.45	1.13	0.59	8155	281
30/123	2.1	9.5	0.5	0.30	0.00	62.67	27.89	0.20	0.16	2.26	0.00	4.33	0.38	0.80	805	273
30/124	2.4	3.3	0.4	1.78	1.00	53.39	24.08	1.29	0.09	13.21	0.08	1.20	1.32	1.86	1613	352
30/156	2.1	6.9	0.3	0.34	0.02	67.41	23.37	0.12	0.08	3.83	0.01	1.41	0.27	1.61	532	270
30/179	5.1	6.8	0.3	0.40	0.03	65.44	28.57	0.04	0.10	1.86	0.00	1.01	0.20	2.23	499	90
30/182	2.6	8.6	0.5	0.18	0.00	77.45	14.93	0.27	1.08	1.39	0.01	1.71	0.89	0.74	3070	319
27/531	0.8	6.9	0.4	2.21	2.05	55.07	23.33	3.21	0.52	4.11	0.01	1.78	3.16	2.52	1350	184
" S1.3		34.9		1.75	0.90	64.23	22.23	1.62	0.18	2.78	0.00	1.28	1.76	3.23	410	52
" F1.3		3.0		2.89	3.93	44.93	26.89	5.58	1.11	6.18	0.00	2.66	5.20	1.70	1810	260
27/531 F1.3-S1.26		13.5		2.22	1.39	53.68	23.54	4.06	0.53	4.51	0.02	1.63	3.25	2.88	1085	101
" F1.26-S1.24		2.4		2.68	4.03	38.50	24.68	6.75	1.48	11.62	0.02	2.99	5.33	1.27	3457	386
" F1.24		1.8		4.00	6.51	25.05	26.42	12.79	0.50	13.52	0.00	2.19	7.34	0.90	1691	492

Table A2.1 continued (Paparoa coals)

PIKE RIVER COALFIELD

Sample	A%ad	MgO	Na2O	SiO2	Al2O3	SO3	P2O5	Fe2O3	MnO	TiO2	CaO	K2O	Sr(ppm)	Ni(ppm)
B 1	6.7	0.38	0.27	34.43	31.53	0.00	0.03	30.96	0.01	0.22	1.44	0.01	315	134
B 2	15.8	0.18	0.15	13.10	7.61	0.97	0.04	73.02	0.00	0.62	0.80	0.31	237	5
B 3	2.0	1.11	2.29	13.81	15.09	7.16	0.03	52.19	0.01	0.38	6.87	0.21	1238	190
B 4	2.6	0.65	1.26	11.18	10.96	4.37	0.02	64.86	0.00	0.16	4.22	0.11	1026	205
B 5	1.7	0.91	0.44	41.97	38.37	5.13	0.04	10.07	0.03	0.62	5.16	0.16	1233	456
B 6	2.0	0.97	0.48	27.80	27.37	1.04	0.01	37.67	0.03	0.20	3.46	0.07	629	343
B 7	2.1	0.72	0.13	29.49	28.95	3.75	0.20	33.91	0.02	0.69	3.25	0.09	786	448
B 8	16.7	0.87	0.22	47.87	37.53	0.29	0.21	1.58	0.02	7.81	0.55	4.69	366	104
B 9	7.8	0.50	0.42	43.10	35.55	0.58	0.06	17.23	0.03	0.25	1.18	0.24	263	87
B 10	2.3	2.12	2.65	1.66	68.73	11.86	0.08	0.41	0.02	0.21	8.27	0.14	3476	175
B 11	5.8	1.26	1.11	42.14	48.53	2.06	1.44	1.14	0.07	0.23	2.98	0.17	5967	82
B 12	4.3	5.16	3.36	32.17	42.46	5.27	0.13	4.23	0.07	0.29	4.95	0.32	930	114
B 13	28.4	2.04	0.27	44.22	46.57	0.17	0.20	0.78	0.04	3.04	0.31	2.65	525	37
B 14	5.3	5.50	2.47	22.65	45.08	6.92	0.89	10.09	0.10	0.24	5.57	0.37	2785	100
"FL4-SL3	6.3	4.03	3.21	27.17	46.13	3.69	1.01	9.28	0.05	0.16	4.56	0.32		
" FL3	3.7	7.76	2.87	15.79	53.03	2.11	0.81	10.10	0.07	0.17	7.76	0.27		
B 15	4.5	4.73	0.33	3.48	76.84	7.26	0.63	2.26	0.06	0.13	5.13	0.44	1714	137
B 16	9.4	1.71	0.63	21.56	63.75	2.29	1.90	0.66	0.05	5.51	2.21	0.87	6440	59
B 17	54.5	0.83	0.15	46.61	48.49	0.08	0.13	0.79	0.00	1.66	0.10	1.91	220	32
B 18	47.5	0.81	0.13	50.27	45.01	0.00	0.10	0.75	0.04	1.37	0.14	1.45	217	50
B 19	3.3	7.12	2.67	14.38	41.93	15.59	0.13	4.67	0.12	0.30	11.04	0.14	2114	188
B 20	21.8	6.38	0.16	2.24	7.16	9.97	0.00	0.21	0.07	0.00	72.38	0.03	10348	33
B 21	12.0	0.44	0.59	19.20	8.91	2.19	0.00	66.08	0.03	0.60	2.60	0.31	1268	16
B 22	8.1	0.64	1.03	7.70	7.37	5.16	0.00	72.26	0.14	0.09	4.32	0.04	1971	48
B 23	56.6	0.44	0.00	54.03	27.28	0.05	0.00	13.51	0.00	3.34	0.34	2.13	98	168

Table A2.2 Ash constituent analyses for Brunner coal: field, run-of-mine, and miscellaneous samples.

GREYMOUTH COALFIELD

Sample	M	A	S	MgO	Na_2O	SiO_2	Al_2O_3	SO_3	P_2O_5	Fe_2O_3	MnO	TiO_2	CaO	K_2O	Sr(ppm)	Ni(ppm)
30/792	0.8	5.3	4.3	11.50	0.56	6.50	2.90	30.80	0.01	26.30	0.14	0.19	21.30	0.30		
30/793	1.3	2.4	0.9	16.20	0.72	4.90	3.30	34.30	0.02	8.30	0.10	0.15	29.60	0.15		
30/927	1.2	4.2	2.8	11.90	0.50	17.00	2.70	22.80	0.02	26.70	0.26	0.12	16.60	0.37		
30/928	1.1	3.1	0.8	20.70	0.32	4.60	1.20	27.80	0.02	9.60	0.25	0.11	32.10	0.18		
33/003	1.1	4.8	3.5	8.20	0.41	21.00	6.40	20.10	0.02	27.70	0.12	0.36	15.10	0.70		
33/004	1.2	3.5	0.8	19.90	0.27	8.40	1.90	22.00	0.02	4.30	0.11	0.13	38.20	0.10		
33/005	1.2	3.0	2.2	18.90	0.38	5.20	1.10	34.60	0.02	9.60	0.16	0.09	28.50	0.13		
33/006	1.2	2.7	0.7	22.40	1.00	2.60	4.00	24.40	0.02	3.80	0.10	0.08	35.70	0.10		
30/948	0.8	3.9	1.6	10.80	0.73	18.90	3.10	29.60	0.02	13.00	0.11	0.26	20.70	0.24		
30/966	0.8	5.5	3.5	17.20	0.52	7.80	2.30	34.10	0.01	8.20	0.10	0.11	26.50	0.33		
33/044	0.9	7.2	4.1	9.20	0.32	25.00	4.40	21.70	0.02	20.70	0.04	0.15	16.40	0.65		
30/971	0.8	7.0	6.3	3.70	0.83	6.60	5.80	22.90	0.02	42.90	0.14	0.28	16.90	0.20		
30/985	0.9	3.1	2.3	14.00	0.73	15.30	3.00	27.80	0.02	16.90	0.19	0.19	20.00	0.48		
33/045	1.2	5.1	0.6	7.00	0.39	57.40	4.30	11.00	0.02	3.50	0.03	0.21	11.00	0.53		
27/545	1.4	12.6	4.0	0.65	1.08	70.90	10.04	1.43	0.02	10.64	0.01	0.38	0.94	2.67	489	32
27/546	1.6	11.5	3.5	0.67	0.60	71.35	9.64	1.55	0.03	8.90	0.01	0.68	1.20	1.94	945	43
27/678	4.8	2.0	2.5	2.76	2.46	40.45	14.95	3.98	0.11	27.31	0.04	0.62	2.64	1.51	3927	80
27/686	2.9	6.7	2.2	0.76	0.69	52.05	20.46	0.86	0.05	18.15	0.02	1.16	0.79	1.98	892	92
27/700	3.7	1.2	1.8	0.95	1.01	22.80	17.57	3.43	0.11	45.80	0.08	0.50	3.53	0.79	2377	103
27/705	2.9	19.7	2.4	0.46	0.08	81.05	5.39	1.23	0.03	6.40	0.03	0.49	0.79	0.70	307	63
27/709	2.6	3.1	0.8	1.66	0.33	58.83	16.08	4.44	0.09	9.61	0.06	0.58	3.41	1.74	2178	177
30/120	1.1	4.6	3.8	3.74	0.25	33.78	5.86	10.59	0.02	34.49	0.08	0.58	8.95	0.61	1700	37
30/121	1.7	3.6	0.8	17.20	0.21	3.18	1.34	26.67	0.02	10.53	0.14	0.09	32.70	0.07	1941	172
30/127	3.2	4.1	3.1	0.63	0.37	56.92	15.15	1.08	0.03	20.19	0.03	0.78	1.14	2.20	991	90
30/128	5.3	3.3	2.3	0.78	0.24	75.32	9.56	2.35	0.05	7.86	0.04	0.51	2.19	0.36		
27/288	3.3	3.0	2.9	2.97	0.85	34.71	9.59	8.33	0.08	35.50	0.30	0.40	7.67	1.20	2563	80
27/289	4.4	8.6	0.7	0.69	0.85	76.21	9.83	1.71	0.05	4.44	0.01	2.32	2.09	0.29	989	142
27/217	3.0	5.0	2.9	1.32	0.64	40.90	7.65	3.61	0.06	38.46	0.14	0.95	3.80	0.60	1496	86
27/224	2.3	2.3	2.5	2.62	3.39	40.46	13.54	6.25	0.15	21.48	0.66	0.83	5.84	1.37	2930	59
30/121 S1.3		23.3		26.16	0.00	3.34	0.85	8.14	0.03	12.14	0.20	0.00	48.62	0.11	1329	19
" F1.3-S1.26		0.4		8.13	1.82	8.00	6.56	29.90	0.24	22.15	0.17	0.48	20.69	0.37	3802	433
" F1.26-S1.24		0.3		6.09	2.45	7.49	7.52	29.56	0.18	20.60	0.09	0.58	20.37	0.32	5877	700
" F1.24		0.4		5.81	2.40	6.62	9.21	30.16	0.10	20.88	0.06	0.57	20.25	0.32	4952	963

Table A2.2 continued (Brunner coals) PIKE RIVER COALFIELD

Table A2.2 continued. (Brunner coals)

Sample	Ash	MgO	Na2O	SiO2	Al2O3	SO3	P2O5	Fe2O3	MnO	TiO2	CaO	K2O	Sr (ppm)	Ni
Buller														
B24	0.3	0.10	2.58	69.37	13.74	1.32	0.03	4.57	0.01	1.09	2.22	0.91	530	477
B25	0.5	1.23	0.57	66.12	11.38	2.53	0.04	9.24	0.03	0.36	2.27	1.34	521	760
B26	61.6	0.87	0.05	50.12	36.86	0.00	0.14	1.31	0.01	1.39	0.03	8.13	141	42
B27S	45.2	0.63	0.11	43.89	45.81	0.18	0.20	2.31	0.00	1.60	0.22	3.77	429	46
B27F	6.0	0.43	0.30	34.11	52.88	1.68	0.38	1.18	0.00	3.73	1.64	2.60	1077	68
B28	0.2	0.94	4.58	52.59	19.35	4.44	0.05	2.81	0.04	3.12	5.00	1.12	926	282
27/510	1.8	0.14	0.68	37.90	26.75	1.67	0.17	29.62	0.02	2.15	1.50	0.53	315	154
27/511	3.6	0.21	0.33	46.03	20.22	1.41	0.26	29.04	0.05	0.84	1.35	0.82	299	103
27/170	1.4	0.52	0.63	44.99	40.73	0.57	0.60	4.36	0.01	1.97	1.56	2.88	337	53
30/349	1.7	0.33	0.42	55.76	15.57	1.80	0.16	19.03	0.01	0.65	1.71	2.96	299	74
29/936	24.4	0.60	0.00	50.30	42.08	0.00	0.20	1.23	0.04	1.85	0.11	4.00	456	42
29/937	2.6	0.00	0.15	46.77	45.05	3.04	0.26	1.91	0.05	3.81	2.87	0.75	464	55
29/939	0.7	0.00	1.20	46.75	40.86	0.79	0.08	8.00	0.03	0.34	1.16	1.21	225	96
29/940	0.3	0.12	2.81	46.18	39.63	0.76	0.07	8.75	0.08	1.02	2.46	0.91	315	151
Reefton-Garvey Creek area.														
B35	7.8	0.61	0.17	44.61	24.21	0.52	3.83	13.91	0.01	1.26	2.59	2.47	6153	101
B36	5.5	0.34	0.66	31.77	26.46	1.99	12.09	6.25	0.02	0.98	16.95	1.40	2381	207
B41	2.1	5.69	1.00	43.56	12.76	11.58	0.14	12.98	0.06	3.18	8.14	0.20	49	31
21/930	1.4	0.82	0.81	43.80	30.50	0.49	0.40	17.20	0.01	0.68	1.50	1.10	n.d.	n.d.
27/503	2.4	1.35	0.56	43.77	19.77	1.72	0.59	25.72	0.02	0.78	2.48	1.68	909	87
30/344	3.4	3.60	0.20	40.63	22.52	7.50	2.20	10.26	0.10	2.26	7.28	1.83	4839	348
B42	3.3	5.69	1.00	43.56	12.76	11.58	0.14	12.98	0.06	3.18	8.14	0.02	5961	122
Flat Creek														
B45	1.6	2.13	0.56	34.04	17.40	2.37	0.82	37.80	0.18	0.63	2.35	1.50	2030	88
Inangahua area														
27/167	3.6	6.81	11.84	5.43	1.99	41.99	0.07	6.59	0.08	0.12	25.24	0.25	4376	70
27/507	3.3	6.56	10.95	12.44	5.10	29.44	0.29	8.19	0.05	0.34	22.16	0.27	6692	64
30/347	4.0	4.85	8.13	18.50	2.70	28.54	0.11	15.06	0.06	0.16	18.83	0.34	4591	52
B48	3.3	4.06	0.00	5.60	8.97	36.38	0.18	1.60	0.13	0.37	29.94	0.16	2050	21
Charleston														
B49	3.3	15.37	0.31	2.88	1.52	51.49	0.04	0.44	0.07	0.10	26.32	0.22	2917	52

Rcd	Sample	DH/Seam	M%ad	A%ad	S%ad	MgO	Na2O	SiO2	Al2O3	SO3	P2O5	Fe2O3	MnO	TiO2	CaO	K2O
1	26/060	619/3	7.5	4.5	0.7	1.30	0.69	53.60	14.30	0.51	0.13	23.50	0.09	0.87	1.90	0.66
2	26/067	619/4	7.8	7.4	0.7	2.10	0.53	59.60	9.60	1.40	0.20	20.10	0.15	0.76	1.70	0.88
3	26/069	619/5	8.4	1.5	0.6	0.98	3.40	42.50	15.80	0.71	0.03	28.10	0.01	0.97	3.90	0.39
4	26/142	621/3	8.4	7.6	0.3	1.70	0.74	70.40	12.20	1.50	0.03	8.40	0.13	1.40	1.60	0.99
5	26/148	621/4	8.4	23.6	0.4	0.75	0.39	72.20	19.10	0.09	0.03	2.00	0.00	1.00	0.29	2.70
6	26/163	622/1	9.0	6.9	0.4	0.54	0.45	83.60	11.00	0.23	0.02	1.58	0.02	1.23	0.70	1.25
7	26/172	622/2	7.0	7.0	0.3	0.24	0.24	81.80	13.10	0.61	0.02	2.19	0.02	0.99	0.75	0.52
8	26/175	622/3	6.7	6.8	0.4	0.53	0.42	71.60	18.80	0.15	0.39	2.81	0.04	0.99	4.15	1.74
9	26/186	622/4	4.8	6.0	0.7	0.89	0.78	48.90	10.11	1.61	0.28	28.20	0.10	0.47	7.66	0.48
10	26/255	623/1	2.6	6.2	0.3	0.88	0.89	71.10	21.10	0.08	0.68	1.61	0.01	1.36	0.82	2.96
11	26/259	623/2	3.3	5.3	0.3	0.83	0.75	62.70	26.70	0.03	1.98	1.68	0.01	1.12	1.63	2.96
12	26/263	623/3	5.7	5.2	0.4	1.50	0.39	47.20	17.40	0.39	3.03	23.40	0.17	0.89	3.80	1.90
13	26/267	623/4	3.6	3.4	0.3	1.26	1.03	45.40	31.20	0.15	5.81	5.82	0.04	1.50	5.09	1.58
14	26/278	624/1	4.2	4.5	0.4	0.32	0.78	67.50	20.00	0.48	0.12	2.80	0.01	3.20	0.48	0.80
15	26/281	624/2	5.4	6.0	0.3	0.39	0.53	68.60	19.00	0.46	0.06	1.50	0.00	2.40	0.21	1.60
16	26/289	624/3	5.3	2.8	0.4	1.00	1.10	62.60	21.90	0.81	0.42	3.60	0.01	2.00	3.40	1.50
17	26/298	624/4	6.4	3.3	0.3	2.50	0.41	35.50	12.20	0.55	0.65	46.60	0.37	1.20	1.40	0.97
18	26/340	626/1	4.5	5.5	0.5	0.67	1.55	69.70	15.70	0.15	0.14	7.64	0.03	2.08	0.95	1.95
19	26/343	626/2	4.4	6.2	0.5	0.27	1.03	79.90	12.20	0.01	0.17	2.04	0.01	1.44	0.86	0.42
20	26/350	626/3	4.4	6.5	0.4	0.49	1.24	78.40	12.80	0.01	0.11	1.78	0.02	1.51	0.85	1.23
21	26/358	626/4	4.9	7.1	0.5	0.47	1.25	79.10	12.20	0.01	0.08	2.65	0.02	1.36	0.82	1.37
22	26/376	628/1	9.9	3.2	0.3	1.40	1.60	55.10	20.00	0.87	0.47	13.80	0.07	1.30	2.20	1.80
23	26/454	630/1	1.6	7.2	0.4	0.62	0.45	69.50	22.00	0.17	0.70	1.12	0.12	3.33	0.46	0.68
24	26/457	630/2	1.5	5.3	0.6	0.31	0.31	66.10	24.70	0.80	0.19	1.20	0.01	1.50	0.71	1.40
25	26/462	630/3	2.2	6.5	0.5	0.53	0.55	62.70	23.80	0.13	3.90	1.24	0.01	1.58	3.17	2.54
26	26/467	630/4	2.0	4.4	0.5	0.71	0.83	57.30	26.30	0.71	1.77	4.80	0.02	1.30	3.00	2.30
27	26/537	631/2	2.3	6.8	0.4	1.44	0.46	65.90	20.30	0.05	0.14	5.90	0.06	1.02	0.52	2.59
28	26/547	631/3	3.7	6.7	0.3	0.85	0.91	56.00	28.00	0.05	2.95	3.13	0.02	1.02	2.17	3.29
29	26/565	631/4	4.6	3.9	0.3	5.00	0.51	41.90	16.30	3.60	0.23	22.20	0.16	0.83	5.20	1.90
30	26/576	631/5	3.2	7.0	0.4	0.87	0.56	58.10	31.10	0.05	1.64	1.60	0.01	1.32	1.55	3.45
31	26/595	631/6	5.4	2.0	0.3	1.40	0.83	52.80	15.10	1.40	0.74	22.20	0.19	1.10	1.60	1.10
32	26/645	632/5	3.7	3.7	0.3	1.90	0.59	24.20	10.70	1.50	0.44	59.80	0.42	0.50	1.70	0.73
33	26/646	632/6	4.3	3.5	0.3	4.60	1.00	10.20	5.60	1.40	0.07	75.60	0.66	0.30	2.00	0.15
34	26/662	633/1	9.3	5.8	0.6	0.58	1.70	70.70	11.20	0.67	0.06	9.20	0.01	0.98	1.80	0.34
35	26/671	635/1	5.7	7.0	0.3	0.49	0.43	72.50	15.10	1.10	0.12	3.40	0.01	1.10	0.69	1.00
36	26/677	635/2	4.0	7.1	0.3	0.57	0.40	72.10	22.00	0.05	0.08	1.14	0.02	2.10	0.25	1.84
37	26/687	635/3	3.9	6.5	0.2	0.69	0.50	71.10	21.40	0.02	0.32	1.38	0.01	1.45	0.45	2.38
38	26/691	635/4	6.9	5.5	0.5	0.49	0.47	71.20	15.20	0.82	0.18	4.10	0.01	1.30	0.71	1.70
39	26/695	635/5	4.4	7.0	1.0	4.74	0.28	31.90	8.01	8.05	0.31	40.60	0.36	0.49	8.15	0.90
40	26/842	636/1	8.1	4.8	0.3	0.67	1.98	77.20	13.80	0.07	0.06	1.52	0.02	2.65	0.81	1.28
41	26/851	636/2	7.5	5.5	0.3	0.53	0.80	82.20	13.70	0.06	0.06	0.89	0.02	1.76	0.54	0.97
42	26/860	636/3	8.1	1.9	0.2	1.95	2.38	60.40	22.10	1.57	0.50	4.57	0.03	1.57	2.72	1.32
43	29/652	638/1	8.6	5.9	0.5	0.61	0.36	70.80	16.10	0.25	0.04	4.20	0.01	3.10	1.20	0.97
44	29/655	638/2	8.1	6.0	0.7	0.56	0.30	74.80	18.80	0.01	0.04	1.34	0.04	2.35	0.38	1.54
45	29/659	638/3	6.2	5.1	0.5	0.95	0.53	67.80	23.50	0.01	0.11	1.91	0.05	1.61	0.37	3.00
46	29/664	638/4	8.4	2.7	0.2	6.20	0.79	40.60	11.90	11.40	0.10	13.40	0.05	1.10	11.80	0.79
47	29/153	639/1	7.6	5.9	0.5	0.76	0.98	76.90	12.10	0.39	0.11	4.30	0.01	1.34	1.33	0.87
48	29/100	640/4	4.5	4.9	0.4	1.01	0.73	63.70	24.00	0.01	1.44	3.62	0.04	1.51	0.90	2.78
49	29/106	640/5	4.9	5.1	0.4	1.16	0.32	64.30	26.20	0.01	0.11	2.54	0.01	1.50	0.24	3.28
50	29/200	641/1	6.0	6.7	0.4	0.68	0.49	74.40	18.10	0.01	0.05	2.26	0.02	2.80	0.61	1.10
51	26/959	642/2	7.1	5.9	0.5	0.54	0.92	74.80	15.40	0.13	0.10	1.85	0.02	3.21	0.75	1.10
52	26/952	642/3	8.3	6.2	0.3	1.09	0.89	68.10	21.20	0.11	0.49	2.28	0.01	1.65	0.87	3.16
53	26/979	643/1	6.5	4.1	0.4	1.10	0.52	45.90	10.40	8.40	0.03	14.20	0.20	1.10	17.30	0.24
54	26/984	643/2	5.5	6.2	0.4	0.36	0.39	69.70	19.70	1.48	0.28	1.97	0.01	1.29	2.39	1.83
55	26/995	643/3	5.9	3.4	0.3	0.28	0.39	70.10	19.80	1.27	0.28	2.06	0.01	1.29	3.02	1.21
56	29/001	643/4	8.4	4.7	0.3	3.40	0.66	36.20	12.30	3.20	0.53	34.50	0.23	0.71	5.30	1.20
57	29/016	644/1(pt)	5.5	4.1	0.4	0.85	2.60	58.80	25.30	0.03	0.67	5.27	0.07	1.96	1.59	2.47
58	29/075	644/1(pt)	5.2	5.6	0.3	0.74	2.41	62.60	23.90	0.34	0.77	2.38	0.06	2.14	1.61	2.26
59	29/037	645/1	5.9	5.9	0.5	0.87	0.61	61.60	16.90	0.83	0.03	12.50	0.09	2.20	1.20	0.46
60	29/040	645/2	5.5	7.4	0.5	0.35	0.55	69.70	14.30	1.60	0.03	4.70	0.01	2.40	1.80	0.48
61	29/046	645/3	4.6	4.8	0.4	0.77	0.66	65.70	23.90	0.13	0.03	3.92	0.07	1.58	0.88	2.33
62	29/047	645/4	5.8	6.5	0.4	0.37	0.27	79.50	15.40	0.01	0.01	1.27	0.04	1.58	0.54	1.24
63	29/053	645/5	5.4	6.0	0.4	0.84	0.34	67.30	24.00	0.01	0.02	2.65	0.06	1.65	0.55	2.94
64	29/061	645/6	6.3	3.5	0.8	0.88	0.46	63.60	19.40	0.18	1.24	8.25	0.09	1.27	1.87	2.20
65	29/026	646/1	9.3	1.7	0.4	0.76	5.40	60.90	20.40	1.40	0.13	3.40	0.02	1.40	2.40	1.60

Table A2.3 Ash constituents analyses (CRA) for drillhole samples of Paparoa coals from the Rapahoe Sector, Greymouth Coalfield.

Rcd	Sample	DH/Seam	M%ad	A%ad	S%ad	MgO	Na2O	SiO2	Al2O3	SO3	P2O5	Fe2O3	MnO	TiO2	CaO	K2O
66	29/033	646/2	9.2	3.4	0.3	1.60	2.30	45.70	12.50	1.30	0.06	33.40	0.26	1.10	2.00	0.3
67	29/674	647/1	7.8	6.0	0.8	0.24	0.41	80.50	11.40	0.01	0.37	4.16	0.03	1.50	1.20	0.1
68	29/685	647/2	7.7	2.9	0.5	0.85	1.01	54.30	12.10	5.80	0.08	12.80	0.05	0.94	8.80	0.6
69	29/696	647/3a	7.6	6.6	0.7	0.24	0.72	82.10	11.20	0.01	0.05	2.64	0.04	1.45	0.65	0.4
70	29/711	647/4	9.5	6.1	1.7	0.51	0.70	54.90	9.90	0.82	0.08	28.20	0.01	0.90	1.60	0.7
71	29/230	648/1	9.8	4.5	0.4	0.37	2.30	73.80	13.80	0.48	0.09	2.50	0.01	1.60	1.70	0.4
72	29/235	648/2	11.4	3.6	0.3	4.50	3.00	33.90	9.70	2.40	0.12	40.00	0.26	0.74	3.40	1.0
73	29/245	650/1	7.2	5.2	1.2	0.97	1.05	45.80	10.20	2.30	1.04	35.30	0.29	1.21	2.71	0.0
74	29/752	656/2	2.8	1.6	0.3	0.88	1.13	51.00	33.30	0.01	2.07	4.15	0.07	2.47	2.04	1.9
75	29/735	656/3	4.3	3.6	0.2	1.70	0.38	50.40	17.00	0.08	0.20	24.80	0.19	0.78	0.79	1.7
76	29/754	656/4	4.7	5.9	0.2	1.20	0.29	58.30	20.50	0.06	0.31	10.40	0.05	0.93	0.61	2.5
77	31/729	657/1	5.3	5.7	0.2	4.40	0.35	21.00	7.10	3.90	0.16	57.80	0.43	0.39	4.50	0.5
78	31/735	657/2	2.9	2.9	0.3	2.50	1.20	53.50	20.90	1.00	1.33	10.40	0.04	0.93	4.50	1.8
79	31/736	657/3	3.3	3.5	0.4	0.81	0.60	72.60	17.00	0.01	0.09	4.20	0.03	1.60	0.41	0.8
80	31/740	657/4	5.5	6.3	0.2	2.90	0.33	55.70	16.60	0.22	0.17	19.90	0.15	2.90	1.10	1.2
81	31/972	658/1	2.5	3.2	0.4	1.20	1.50	60.80	22.20	0.13	0.46	7.90	0.02	1.60	1.30	1.7
82	31/779	658/2	3.5	6.3	0.3	2.50	0.67	36.30	17.30	3.40	0.95	31.80	0.16	0.81	6.60	1.2
83	31/800	658/7	2.1	2.7	0.3	0.64	1.25	60.80	26.70	0.01	0.19	4.11	0.03	1.49	1.31	1.8
84	31/847	659/3	1.3	6.7	0.4	0.59	0.31	65.60	22.90	0.01	1.56	2.16	0.04	3.33	1.44	1.5
85	32/008	660/2	1.1	6.5	0.3	0.64	1.01	62.20	22.30	0.01	1.99	3.45	0.04	3.61	1.67	1.8
86	32/013	660/3	1.5	4.1	0.4	1.10	0.66	58.40	20.90	0.15	0.33	13.40	0.08	1.40	0.82	1.5
87	34/372	662/1	2.6	6.5	0.3	1.27	0.14	47.70	29.40	0.01	3.04	9.21	0.14	1.54	2.05	4.4
88	34/370	662/2(pt)	3.5	4.4	0.3	1.03	0.46	51.60	32.50	0.11	3.22	1.82	0.08	1.76	4.21	2.0
89	34/371	662/2(pt)	4.3	5.5	0.3	2.60	0.27	36.80	18.30	0.15	1.00	35.90	0.25	0.71	1.30	2.3
90	34/375	663/1	2.3	5.0	0.3	1.24	0.65	59.60	28.10	0.15	2.68	2.11	0.06	1.55	1.94	3.3
91	34/374	663/2	4.5	2.3	0.3	2.30	0.74	34.30	10.80	0.28	0.01	47.10	0.41	0.73	1.00	0.2
92	34/373	663/3	3.8	5.9	0.3	1.01	0.67	68.30	17.20	0.10	0.14	7.99	0.12	1.24	0.41	2.2
93	35/055	664/1	2.9	3.9	0.2	2.00	0.49	39.40	13.40	0.51	0.45	40.20	0.22	0.86	0.77	1.3
94	35/057	664/2(pt)	2.7	5.8	0.3	3.07	0.44	47.10	21.60	2.05	2.80	13.00	0.20	1.01	5.99	2.5
95	35/056	664/2(pt)	4.0	4.3	0.3	2.80	0.36	39.30	14.60	0.08	0.73	37.60	0.30	1.10	1.60	0.7
96	35/058	665/1	3.3	6.2	0.3	2.00	0.30	48.00	20.20	0.10	1.70	19.20	0.14	0.95	2.20	2.8
97	35/059	665/2	2.5	3.6	0.4	1.16	0.36	55.10	25.40	0.21	0.59	12.30	0.15	1.65	0.68	2.4
98	35/060	665/3	2.6	3.7	0.3	1.80	0.56	28.20	19.60	0.14	0.76	43.80	0.34	0.64	1.40	1.6
99	35/061	666/1	2.2	6.2	0.3	1.66	0.19	48.40	25.10	0.67	2.90	14.30	0.18	1.15	2.07	3.4
100	35/062	666/2(pt)	2.4	5.9	0.3	2.04	0.26	57.80	19.00	0.27	0.19	16.40	0.17	1.02	0.54	2.5
101	35/064	666/2(pt)	2.1	5.8	0.3	1.36	0.25	53.40	20.70	0.25	1.80	16.90	0.20	1.53	1.26	2.2
102	35/063	666/2(pt)	3.3	6.5	0.3	2.10	0.26	43.30	19.80	0.11	1.32	28.00	0.23	0.81	1.20	2.4
103	35/231	667/1	4.2	5.7	0.2	2.40	0.44	54.90	23.30	1.60	2.03	6.70	0.03	0.93	3.80	2.9
104	35/230	667/2	5.2	2.2	0.2	2.60	0.83	53.90	12.10	0.28	0.28	26.20	0.17	0.78	1.20	0.6

Table A2.3 continued.

Rcd	Sample	DH/Comp.	M%ad	A%ad	S%ad	MgO	Na2O	SiO2	Al2O3	SO3	P2O5	Fe2O3	MnO	TiO2	CaO	K2O
1	31/050	UG3/2	2.1	0.4	0.6	0.37	2.40	39.20	27.80	0.23	0.64	22.60	0.02	1.00	2.30	1.10
2	31/051	UG3/1	2.1	1.9	0.5	0.12	0.33	46.50	43.30	0.36	0.19	4.40	0.00	0.18	0.84	0.22
3	31/056	UG5/1	1.1	31.4	0.9	0.62	0.10	48.70	42.50	0.00	0.14	2.50	0.00	1.60	0.12	3.10
4	31/057	UG5/2	1.2	3.5	1.1	0.35	0.21	44.60	43.00	0.00	0.12	7.40	0.01	1.90	0.38	1.30
5	31/058	UG5/3	1.2	1.3	1.9	0.18	0.36	47.90	44.00	0.53	0.07	3.00	0.01	2.40	1.10	0.38
6	31/061	UG7/1	1.3	7.6	2.5	0.57	0.13	46.00	37.10	0.00	0.25	9.50	0.01	1.40	0.39	3.40
7	31/062	UG7/2	1.4	0.4	1.2	0.29	2.20	35.60	35.40	0.99	0.13	18.00	0.01	1.50	2.50	1.80
8	31/063	UG7/3	1.0	4.0	3.4	0.20	0.20	46.90	40.80	0.00	0.14	3.40	0.00	2.80	0.52	3.40
9	31/064	UG8/1	1.3	0.4	1.6	0.47	2.60	34.20	33.30	1.10	0.42	21.60	0.04	1.30	2.60	0.67
10	31/065	UG8/2	0.8	3.6	4.4	0.13	0.35	45.30	41.50	0.42	0.88	4.80	0.02	1.40	2.20	0.59
11	31/059	F2/1	2.7	1.2	1.9	0.28	0.61	47.40	41.60	0.55	0.17	2.00	0.01	1.90	1.10	2.20
12	31/060	F2/2	2.0	0.5	2.5	0.25	3.00	45.60	38.20	2.00	0.15	2.00	0.01	1.30	2.20	2.70
13	31/086	F3/1	1.4	0.3	1.5	0.15	2.40	25.50	21.60	1.20	0.15	41.90	0.03	0.93	1.90	1.10
14	31/087	F3/2	1.0	1.4	3.1	0.07	0.45	47.80	42.70	0.38	0.04	5.30	0.02	0.78	0.80	0.84
15	31/044	1215/1	0.9	0.9	4.2	0.23	0.62	27.80	29.80	2.30	0.11	32.60	0.08	2.30	3.10	0.73
16	31/045	1215/2	1.0	11.1	2.0	0.59	0.18	47.70	40.70	0.17	0.49	1.70	0.00	2.50	0.79	3.80
17	31/046	1215/3	1.0	11.4	2.1	0.24	0.13	47.40	41.20	0.24	0.14	0.77	0.01	2.10	0.51	3.90
18	31/047	1215/4	1.0	3.7	1.6	0.30	0.35	46.90	42.00	0.16	0.20	1.20	0.00	3.70	0.63	3.70
19	31/048	1215/5	1.3	1.1	2.6	0.18	1.50	48.80	40.20	0.39	0.04	0.92	0.00	0.86	1.10	3.70
20	31/049	1215/6	1.0	18.6	3.5	0.38	0.17	50.30	41.10	0.19	0.27	1.80	0.00	2.20	0.36	2.70
21	31/040	1216/1	0.8	4.0	1.0	0.51	0.26	45.80	41.90	0.48	0.24	2.80	0.01	1.90	1.00	2.40
22	31/041	1216/2	0.9	0.5	2.5	0.20	2.30	44.30	34.80	0.79	0.12	10.90	0.02	1.20	2.10	2.00
23	31/113	1218/1	1.4	6.5	1.1	0.36	0.14	65.10	20.70	0.04	0.07	4.50	0.01	0.92	0.26	3.80
24	31/114	1218/2	1.2	2.6	2.9	0.13	0.48	63.20	26.70	0.21	0.35	4.70	0.01	0.54	0.68	1.20
25	31/069	1220/1	1.2	0.2	1.4	0.30	3.10	38.80	23.40	2.50	0.07	23.50	0.04	1.30	3.80	0.95
26	31/070	1220/2	0.8	2.4	4.2	0.16	0.58	47.30	43.40	0.23	0.38	4.80	0.03	0.48	1.40	0.40
27	31/083	1222/1	1.0	4.6	2.8	0.47	0.24	47.20	37.50	0.05	0.20	9.60	0.01	1.50	0.36	2.60
28	31/084	1222/2	1.1	0.3	1.1	0.36	1.80	53.40	32.20	0.45	0.08	4.80	0.01	1.10	1.40	2.20
29	31/085	1222/3	0.8	4.8	3.8	0.28	0.33	47.70	40.60	0.00	0.11	5.00	0.01	1.90	0.24	2.50
30	31/075	1226/1	1.2	4.0	1.0	0.30	0.22	51.60	39.30	0.02	0.50	3.10	0.00	1.20	0.66	1.70
31	31/076	1226/2	0.9	0.1	0.7	0.35	1.70	43.70	35.20	1.80	0.11	9.80	0.02	1.00	2.40	1.10
32	31/077	1226/3	1.1	0.5	0.7	0.26	1.30	34.40	49.60	0.60	1.30	6.90	0.01	0.79	1.20	1.20
33	31/078	1226/4	1.2	0.3	0.9	0.24	3.70	35.40	44.20	1.10	1.70	5.60	0.02	1.50	3.40	0.89
34	31/079	1226/5	1.7	0.1	1.6	0.16	3.60	31.60	45.10	2.40	2.20	5.70	0.02	2.00	4.00	1.00
35	31/080	1226/6	1.2	0.3	3.0	0.16	2.10	34.70	28.80	1.10	0.36	25.80	0.02	1.20	1.90	0.72
36	31/081	1226/7	2.3	1.2	3.4	0.10	0.43	36.60	36.90	0.85	0.72	21.70	0.01	0.54	0.72	0.48
37	31/082	1226/8	1.0	3.8	3.8	0.12	0.24	47.10	41.70	0.03	1.80	1.30	0.01	0.56	5.30	0.35
38	31/088	1227/1	1.1	33.5	0.5	0.64	0.11	47.00	39.70	0.00	0.13	1.60	0.00	1.50	0.04	3.10
39	31/089	1227/2	1.3	1.6	0.7	0.29	0.26	50.60	39.80	0.64	0.08	4.90	0.01	1.30	0.94	1.10
40	31/090	1227/3	1.1	0.9	2.0	0.13	0.53	34.30	27.40	0.01	0.16	30.40	0.01	1.20	0.77	1.30
41	31/071	1228/1	1.0	36.3	0.6	0.66	0.10	46.90	44.30	0.00	0.18	1.60	0.00	1.40	0.04	2.90
42	31/072	1228/2	1.1	2.0	0.7	0.12	0.14	50.50	41.80	0.01	0.03	4.00	0.01	0.31	0.42	0.33
43	31/073	1228/3	1.0	0.5	1.5	0.13	0.83	26.60	19.00	0.53	0.05	47.40	0.01	0.67	0.91	0.42
44	31/074	1228/4	0.8	1.8	4.6	0.08	0.35	12.70	9.20	0.25	0.02	73.00	0.03	0.30	0.78	0.11
45	31/106	1232/1	1.2	2.6	1.7	0.20	0.27	44.80	36.40	0.01	0.16	12.50	0.01	1.10	0.46	1.20
46	31/107	1232/2	0.7	13.5	3.5	0.27	0.15	48.60	38.10	0.00	0.06	5.10	0.01	2.40	0.45	2.50
47	31/095	1234/1	0.9	4.7	3.1	0.18	0.16	44.10	38.20	0.21	0.27	11.10	0.01	1.60	0.82	1.60
48	31/109	1235/1	1.1	2.8	2.4	0.13	0.55	35.50	40.00	0.13	0.09	19.10	0.02	0.59	0.62	1.80
49	31/103	1236/1	1.1	2.1	3.0	0.30	0.11	46.80	36.50	0.10	0.41	7.70	0.01	1.80	0.62	3.40
50	31/104	1236/2	1.3	0.4	1.4	0.33	1.70	33.60	29.70	1.30	0.18	24.10	0.01	0.89	1.90	3.10
51	31/105	1236/3	1.1	1.5	2.5	0.27	0.52	37.20	37.20	0.22	0.57	16.30	0.01	0.54	0.80	4.40
52	31/110	1241/1	2.6	1.6	3.6	0.70	0.34	13.50	15.50	2.70	0.24	57.90	0.02	0.41	2.70	1.40
53	31/111	1241/2	1.1	0.4	1.1	0.34	0.60	27.00	10.80	1.70	0.09	51.40	0.02	0.55	3.00	1.80
54	31/112	1241/3	0.9	2.8	3.8	0.15	0.14	28.40	18.00	0.17	0.10	48.40	0.01	0.29	0.76	3.10
55	31/039	UG1/1	1.7	0.5	1.4	0.43	2.30	38.70	36.30	0.49	0.00	14.90	0.02	0.37	1.80	1.80
56	31/052	UG4/1	1.1	21.4	1.0	0.59	0.10	50.40	40.00	0.01	0.24	2.70	0.01	1.70	0.37	3.30
57	31/053	UG4/2	1.2	1.9	1.0	0.25	0.29	47.40	41.90	0.54	0.22	3.70	0.01	2.10	1.40	1.60
58	31/054	UG4/3	1.4	0.5	1.4	0.23	1.40	45.60	40.10	1.30	0.06	4.40	0.02	1.80	2.50	1.20
59	31/055	UG4/4	0.8	6.9	3.0	0.27	0.16	47.80	42.30	0.64	0.28	2.10	0.02	2.80	0.88	1.90
60	31/043	UG6/1	1.1	1.5	2.2	0.07	0.57	43.50	38.80	0.63	0.04	13.30	0.01	1.20	1.10	0.31

Table A2.4 Ash constituents analyses (CRA) for drillhole samples of Brunner coal from Webb/Baynes, Buller Coalfield.

Rcd	Sample	DH/Seam	M%ad	A%ad	S%ad	MgO	Na2O	SiO2	Al2O3	SO3	P2O5	Fe2O3	MnO	TiO2	CaO	K2O
61	31/066	UG9/1	1.0	13.4	1.5	0.51	0.13	47.60	38.40	0.35	0.19	5.30	0.01	1.80	0.47	3.10
62	31/067	UG9/2	1.2	0.3	2.0	0.31	1.40	33.00	33.20	1.20	0.25	24.10	0.02	1.00	2.20	1.00
63	31/068	UG9/3	0.8	2.7	4.0	0.19	0.42	45.40	40.20	1.20	0.22	5.30	0.05	1.70	1.90	1.10
64	31/031	OC1/1	1.4	1.7	3.5	0.25	0.29	37.20	29.30	0.40	0.70	22.80	0.02	3.10	2.50	2.00
65	31/032	OC1/2	1.9	0.2	1.2	0.29	4.20	30.60	20.20	3.60	0.00	30.10	0.03	2.00	4.00	1.40
66	31/216	OC3/1	8.4	1.2	1.9	2.20	1.70	23.50	53.90	6.70	0.18	4.60	0.03	0.87	3.50	0.95
67	31/108	OC4/1	7.6	1.5	3.0	1.10	1.70	16.80	38.60	3.90	0.14	28.50	0.01	0.59	2.00	2.10
68	31/042	F1	1.3	0.4	2.9	0.32	2.80	39.30	31.90	1.30	0.08	17.20	0.02	1.20	2.50	1.90
69	31/094	F4	1.5	0.2	1.1	0.15	3.60	34.60	40.70	1.80	0.92	8.80	0.03	1.20	3.40	1.50
70	31/134	1213A/1	0.9	10.5	1.2	0.41	0.15	48.20	42.50	0.24	0.16	1.70	0.01	2.10	0.52	3.60
71	31/033	1214/1	0.9	14.1	1.2	0.47	0.19	42.50	47.30	0.27	0.30	1.20	0.01	1.80	0.55	3.30
72	31/034	1214/2	0.8	2.9	2.6	0.10	0.33	36.10	49.50	1.00	0.43	5.60	0.02	1.90	1.40	0.81
73	31/130	1217/1	2.3	5.6	1.8	0.36	0.25	63.90	24.80	0.22	0.09	4.40	0.01	1.40	0.42	3.10
74	31/131	1217/2	1.3	0.6	0.8	0.23	2.10	63.60	20.50	1.20	0.05	4.90	0.02	1.00	1.30	2.80
75	31/132	1217/3	1.2	2.3	1.9	0.16	0.63	76.90	11.00	0.16	0.23	3.60	0.02	0.46	0.38	2.60
76	31/133	1217/4	1.0	1.1	3.6	0.15	1.50	67.60	16.00	0.99	0.06	8.60	0.05	0.92	1.10	1.90
77	31/116	1219/1	1.4	11.8	4.2	0.41	0.10	44.60	34.50	0.00	0.13	16.10	0.01	1.10	0.24	3.10
78	31/117	1219/2	1.4	1.0	1.5	0.05	0.22	33.50	27.30	0.15	0.09	33.70	0.01	3.10	0.89	0.48
79	31/118	1219/3	1.6	0.4	1.4	0.09	1.90	23.50	16.50	0.66	0.06	51.00	0.00	0.85	1.40	0.69
80	31/119	1221/1	1.5	2.6	3.3	0.34	0.48	15.80	13.70	5.70	0.18	47.50	0.04	0.87	1.80	11.40
81	31/120	1221/2	1.1	0.3	0.9	0.37	3.10	36.00	19.10	10.30	0.29	14.60	0.04	1.30	4.50	7.30
82	31/121	1221/3	0.9	1.7	3.9	0.09	0.48	24.20	15.90	0.33	0.04	52.20	0.02	0.37	0.87	1.90
83	31/099	1223/1	1.0	1.4	3.3	0.18	0.22	23.70	9.50	0.16	0.12	61.70	0.02	0.49	0.64	1.30
84	31/100	1223/2	1.1	0.2	1.6	0.70	2.00	45.20	27.80	2.90	0.12	10.80	0.03	0.96	4.20	2.90
85	31/091	1224/1	3.2	0.2	0.8	0.83	1.70	43.70	30.50	1.20	0.57	11.50	0.02	1.40	3.10	1.90
86	31/092	1224/2	5.0	0.2	0.6	1.40	2.20	29.70	26.40	0.00	0.36	24.50	0.05	1.10	3.20	1.80
87	31/093	1224/3	6.9	0.4	1.0	0.59	1.70	32.90	33.10	2.80	0.15	16.40	0.03	0.88	2.10	1.80
88	31/143	1225A/1	0.8	1.0	0.9	0.19	0.19	46.50	35.60	0.09	0.24	14.30	0.01	0.87	0.79	1.70
89	31/144	1225A/2	1.0	1.4	0.7	0.69	0.37	61.90	24.20	0.00	0.22	5.20	0.01	0.97	0.74	4.10
90	31/145	1225A/3	0.9	0.8	0.6	0.55	0.38	57.20	29.00	0.16	0.31	5.70	0.01	1.00	1.10	3.60
91	31/146	1225A/4	1.0	2.4	0.6	0.36	0.40	55.90	35.40	0.02	0.12	3.60	0.01	0.47	0.61	2.40
92	31/096	1229/1	1.0	8.5	0.8	0.26	0.10	48.50	39.70	0.00	0.21	4.30	0.01	2.40	0.37	2.30
93	31/097	1229/2	1.2	0.3	0.8	0.16	1.90	25.90	19.00	1.50	0.06	46.10	0.02	1.10	2.50	0.73
94	31/098	1229/3	1.2	0.1	0.8	0.44	3.40	44.00	31.40	2.10	0.09	8.10	0.03	2.00	4.40	2.10
95	31/970	1229A/1	1.2	0.2	1.4	0.13	0.80	29.90	21.60	0.88	0.14	43.30	0.02	0.85	1.60	0.78
96	31/971	1229A/2	0.9	3.0	4.0	0.10	0.16	44.40	29.10	0.12	0.06	23.70	0.03	0.57	0.66	0.73
97	31/135	1230/1	1.2	5.6	0.6	0.31	0.10	51.40	41.50	0.00	0.19	1.70	0.01	2.40	0.22	2.00
98	31/136	1230/2	1.2	0.7	1.2	0.23	0.61	38.20	28.70	0.06	0.10	30.30	0.01	0.94	0.80	1.10
99	31/137	1230/3	1.1	3.2	4.0	0.06	0.18	33.20	27.70	0.01	0.05	38.40	0.01	0.34	0.31	0.33
100	31/122	1231B/1	1.0	4.7	0.9	0.41	0.19	50.30	41.80	0.00	0.19	2.40	0.01	1.20	0.39	2.80
101	31/123	1231B/2	1.2	0.6	1.5	0.39	1.80	42.60	30.20	0.29	0.13	19.80	0.01	1.40	1.10	2.50
102	31/124	1231B/3	1.1	2.1	4.1	0.24	0.52	34.30	24.20	0.17	0.25	36.30	0.03	1.00	0.73	1.80
103	31/115	1233/1	1.4	0.3	1.0	0.23	1.00	53.10	14.30	0.46	0.09	27.00	0.02	0.74	1.30	1.30
104	31/138	1233A/1	1.3	2.0	1.6	0.37	0.36	52.30	23.80	0.01	0.20	19.90	0.01	0.99	0.55	2.10
105	31/147	1237/1	1.9	3.5	2.5	0.23	0.30	73.80	16.10	0.11	0.18	3.60	0.01	0.58	0.60	3.20
106	31/148	1237/2	1.1	0.7	1.5	0.18	0.79	68.50	14.80	0.13	0.15	7.90	0.01	0.79	0.96	2.60
107	31/149	1237/3	1.0	4.0	3.9	0.07	0.19	43.20	36.00	0.00	0.07	18.60	0.02	0.33	0.50	1.00
108	31/968	1238/1	1.1	2.2	3.6	0.19	0.21	22.30	15.80	0.01	0.15	55.60	0.03	0.90	0.70	1.70
109	31/969	1238/2	1.3	0.3	1.5	0.15	4.30	34.70	33.00	0.92	1.48	17.40	0.08	1.20	3.00	1.30
110	31/128	1239/1	0.7	2.7	1.7	1.80	0.71	33.00	41.70	7.10	0.21	3.40	0.08	3.20	6.10	2.00
111	31/129	1239/2	1.1	1.5	1.2	0.62	0.52	44.00	34.40	1.80	0.12	10.80	0.03	1.10	2.50	3.00
112	31/101	1242/1	1.0	0.8	2.7	0.15	0.51	27.90	13.70	0.50	0.06	53.10	0.02	0.77	0.83	0.84
113	31/102	1242/2	0.8	14.8	4.2	0.29	0.12	46.40	37.50	0.02	0.20	8.10	0.00	1.70	0.64	3.40
114	31/141	1243/1	1.1	1.1	2.1	0.25	0.67	22.50	13.80	0.10	0.09	52.30	0.01	0.41	0.76	0.56
115	31/142	1243/2	0.8	5.0	4.1	0.08	0.15	44.10	37.10	0.06	0.26	15.30	0.01	0.87	0.56	1.30
116	31/140	1244/1	1.1	5.2	3.0	0.15	0.14	60.00	24.90	0.14	0.28	11.60	0.01	0.81	0.59	1.50

Table A2.4 continued.

Rcd	Sample	DH/Seam/Comp.	M%ad	A%ad	S%ad	MgO	Na2O	SiO2	Al2O3	SO3	P2O5	Fe2O3	MnO	TiO2	CaO	K2O
1	32/596	1182/1	5.2	2.1	0.6	0.33	0.32	56.70	32.50	0.18	0.14	2.60	0.01	1.30	0.76	1.10
2	32/528	1183/1	4.4	2.2	2.3	0.18	0.48	43.60	23.30	0.23	0.30	28.70	0.01	2.00	0.67	1.00
3	32/529	1183/2	3.9	14.5	1.1	0.75	0.19	61.90	25.80	0.00	0.76	2.30	0.01	2.50	1.10	4.20
4	32/525	1189/1	6.3	0.6	0.6	0.21	0.32	33.30	21.40	0.02	0.17	41.40	0.01	0.42	1.30	0.38
5	32/526	1189/2	5.4	19.8	0.3	0.61	0.22	51.10	39.00	0.00	0.17	1.20	0.00	2.20	0.33	4.00
6	32/527	1189/3	5.6	10.7	0.8	0.67	0.22	51.00	38.50	0.01	0.17	2.30	0.00	2.20	0.35	4.00
7	32/244	1190/1	5.9	13.3	3.4	0.72	0.20	46.60	40.20	0.64	0.00	2.00	0.00	2.40	1.00	3.50
8	32/597	1191A/1	1.5	3.8	5.2	0.28	0.45	37.40	15.80	0.17	0.11	40.40	0.02	0.60	0.59	2.60
9	32/521	1195/1	7.0	0.6	0.6	0.72	0.49	57.00	27.20	0.47	0.27	5.40	0.01	1.20	1.70	2.30
10	32/192	1195/3	6.8	3.5	0.6	0.30	0.45	46.10	37.20	0.23	1.74	1.70	0.01	5.20	3.30	0.78
11	32/522	1196/1	7.2	1.8	1.2	0.42	0.41	42.20	18.10	0.25	0.68	31.60	0.02	0.86	1.70	1.30
12	32/523	1196/2	7.7	8.2	0.7	0.30	0.20	45.10	32.20	0.20	5.34	1.70	0.01	3.00	8.10	1.60
13	32/524	1196/3	6.8	1.9	0.9	0.27	0.32	62.50	19.00	0.87	0.87	7.10	0.02	1.50	3.10	0.58
14	32/301	1197/1	4.1	7.2	2.3	1.30	0.88	58.80	9.80	0.18	0.10	22.60	0.04	0.55	0.54	1.60
15	32/598	1197/2	5.9	1.0	1.0	0.36	0.34	36.10	11.90	0.17	0.04	45.70	0.02	0.87	0.56	0.34
16	32/306	1197/3	5.6	5.7	0.9	0.31	0.22	62.30	19.40	0.00	0.58	6.10	0.01	3.90	0.98	1.70
17	32/599	1199/1	2.3	6.3	4.3	0.32	0.38	37.30	33.60	0.00	0.30	19.20	0.02	2.50	0.38	2.90
18	32/600	1201/1	4.6	2.1	2.8	0.20	0.22	14.10	5.70	0.21	0.01	61.30	0.04	0.36	1.00	0.50
19	32/395	1201/2	5.0	0.8	1.7	0.16	0.36	11.10	7.50	0.09	4.40	66.60	0.04	0.40	1.20	0.21
20	32/394	1201/3	4.8	4.0	2.1	0.38	0.28	40.40	31.30	0.16	6.40	2.10	0.01	2.10	10.70	1.70
21	32/386	1201/4	5.2	5.1	3.8	0.21	0.16	42.90	34.20	0.00	1.60	12.60	0.01	3.70	2.80	0.76
22	35/752	1276/1	3.5	5.5	6.4	0.00	0.14	2.60	1.50	0.00	0.12	92.30	0.01	0.03	0.12	0.03
23	35/753	1276/2	4.2	0.6	1.2	0.12	0.52	45.60	25.00	0.09	0.06	25.50	0.00	0.53	1.10	0.14
24	35/754	1276/3	3.9	6.0	0.8	0.50	0.21	55.40	33.70	0.05	0.18	1.40	0.00	5.00	0.32	2.10
25	35/327	1277/1	3.9	3.1	4.8	0.22	0.31	20.80	12.60	0.00	0.13	63.80	0.00	0.09	0.35	0.09
26	35/328	1277/2	3.8	0.7	2.9	0.17	0.74	16.10	9.30	0.34	0.26	68.50	0.02	0.55	0.89	0.17
27	35/329	1277/3	4.5	0.4	1.4	0.34	0.26	40.80	10.20	0.02	0.26	43.10	0.02	0.55	1.00	0.20
28	35/330	1277/4	4.5	1.8	1.1	0.08	0.02	67.30	23.60	0.00	0.23	4.80	0.00	1.00	0.67	0.06
29	35/759	12708/1	1.8	31.9	3.1	0.43	0.14	45.70	42.30	0.01	0.00	5.30	0.00	1.50	0.67	3.00
30	35/760	12708/2	1.7	34.3	2.6	0.63	0.20	47.30	40.90	0.00	0.00	5.60	0.01	1.80	0.31	2.80
31	35/761	12708/3	2.2	19.2	1.9	0.38	0.16	45.70	38.40	0.11	1.80	6.10	0.00	2.00	2.60	2.00
32	35/482	1279/2	5.2	0.8	0.4	0.19	0.87	61.20	27.80	0.00	0.10	2.60	0.01	2.10	0.72	0.47
33	35/762	1280/1	2.3	11.8	2.9	0.19	0.18	39.20	33.90	0.17	4.00	12.50	0.00	1.40	6.80	1.50
34	35/763	1281/1	3.1	1.5	4.5	0.03	0.74	20.90	8.20	0.52	0.17	65.90	0.02	0.34	0.94	0.48
35	35/764	1281/2	4.8	0.7	3.0	0.11	0.70	20.20	10.60	0.23	0.18	63.70	0.02	0.50	1.00	0.45
36	35/765	1281/3	5.1	0.4	0.8	0.01	0.45	44.20	28.10	0.01	0.11	22.50	0.00	1.80	1.10	0.19
37	35/766	1281/4	5.0	4.0	0.6	0.13	0.17	69.50	22.40	0.00	0.50	0.78	0.01	2.80	0.67	0.50
38	35/484	1282/1	4.5	2.0	0.7	0.22	0.18	54.20	35.60	0.00	1.10	1.60	0.01	2.80	1.90	0.63
39	35/485	1282/2	4.8	0.4	0.4	0.19	0.19	47.30	41.30	0.00	0.21	4.80	0.01	0.40	2.40	0.19
40	35/486	1282/3	4.0	3.8	0.3	0.01	0.06	48.60	44.00	0.00	2.10	0.70	0.00	0.19	4.30	0.05
41	35/487	1282/4	2.7	33.4	0.3	0.24	0.12	49.20	42.70	0.00	0.00	1.20	0.01	1.40	0.28	2.90
42	35/488	1282/5	5.5	4.6	0.3	0.21	0.10	47.60	45.70	0.00	0.67	1.20	0.00	1.50	0.92	1.10
43	35/489	1282/6	3.8	0.6	0.4	0.11	0.12	51.40	42.40	0.00	0.11	2.30	0.00	1.20	0.97	0.21
44	35/490	1282/7	3.6	4.5	0.5	0.17	0.09	56.10	32.00	0.00	2.30	1.30	0.01	2.10	4.30	1.40
45	35/305	1285/1	3.4	4.0	4.6	0.15	0.16	15.30	6.10	0.16	0.26	74.20	0.00	0.28	0.36	1.20
46	35/306	1285/2	2.4	3.4	5.8	0.04	0.31	25.70	16.70	0.36	0.63	50.40	0.01	2.10	1.60	0.43
47	35/307	1285/3	2.2	14.4	5.1	0.25	0.12	50.30	20.80	0.02	0.70	20.50	0.03	3.20	1.10	1.20
48	35/308	1286/1	4.9	0.9	0.8	0.37	0.26	46.50	21.10	0.09	0.18	26.00	0.00	0.70	0.92	1.90
49	35/309	1286/2	4.9	0.1	0.4	1.10	0.91	40.10	20.00	1.30	0.49	22.70	0.04	1.20	8.00	1.20
50	35/313	1287/1	2.6	14.5	2.8	0.47	0.09	44.00	20.70	0.44	1.36	11.60	0.01	1.80	2.20	3.10
51	35/315	1288/1	2.4	4.0	4.5	0.39	0.38	38.60	30.20	0.12	1.28	20.70	0.01	2.40	0.71	5.20
52	35/316	1288/2	1.5	9.5	4.5	0.54	0.32	46.10	36.40	0.16	1.36	6.60	0.01	2.30	2.20	3.60
53	35/317	1289/1	2.3	3.2	3.3	0.40	0.43	25.00	12.70	0.20	0.19	57.40	0.01	0.27	1.30	1.60
54	35/318	1289/2	11.0	1.2	0.8	1.20	1.50	36.90	50.00	0.50	0.17	4.80	0.00	0.60	1.30	0.68
55	35/319	1289/3	11.5	1.2	0.8	1.20	1.60	35.70	49.60	0.81	0.15	5.40	0.00	0.63	1.40	1.20
56	35/320	1290/1	4.7	5.2	1.7	0.63	0.23	40.70	32.70	0.02	2.10	15.00	0.00	2.30	3.60	2.60
57	35/321	1290/2	4.6	3.1	1.5	0.61	0.11	44.30	27.60	0.22	4.60	7.10	0.01	2.00	8.40	4.80
58	35/483	1294/1	6.9	2.1	0.8	0.34	0.16	44.80	34.20	0.00	0.16	14.70	0.02	2.00	0.44	1.70
59	35/323	1295/1	3.1	6.4	6.2	0.26	0.08	34.70	11.00	0.10	0.32	51.10	0.00	0.53	0.36	0.75
60	35/324	1296/1	8.9	1.4	1.0	0.60	0.23	19.60	31.00	0.19	0.34	44.80	0.00	0.19	0.51	0.35

Table A2.5 Ash constituents analyses (CRA) for drillhole samples of Brunner coal from the Upper Waimangaroa Sector, Buller Coalfield.

Rcd	Sample	DH/Seam	M%ad	A%ad	S%ad	MgO	Na2O	SiO2	Al2O3	SO3	P2O5	Fe2O3	MnO	TiO2	CaO	K2O
61	35/325	1296/2	7.1	0.6	0.6	1.50	0.31	46.80	22.30	0.01	0.60	23.60	0.01	0.57	1.20	0.25
62	35/326	1296/3	5.8	3.6	0.7	0.10	0.13	66.00	20.10	0.00	0.42	7.00	0.01	1.50	0.26	1.30
63	35/767	1334/1	4.9	2.6	2.3	0.24	0.27	26.70	16.50	0.88	2.70	43.90	0.02	1.70	3.70	1.60
64	35/768	1334/2	2.3	6.6	5.0	0.09	0.14	32.50	6.80	17.80	0.22	21.00	0.11	2.10	17.10	0.74
65	35/769	1334/3	2.9	11.6	4.9	0.40	0.19	40.00	30.70	4.00	3.14	8.00	0.03	2.00	8.30	2.40
66	35/770	1335/1	2.8	10.4	10.4	0.27	0.14	8.80	6.40	0.17	0.62	84.90	0.05	0.26	0.43	0.15
67	35/771	1335/2	2.2	2.8	4.9	0.10	0.56	23.70	17.00	0.13	1.00	53.10	0.03	1.20	1.70	0.41
68	35/772	1335/3	1.7	28.1	3.4	0.39	0.12	50.60	38.10	0.00	4.20	2.80	0.01	0.88	1.80	3.00
69	35/773	1335/4	2.5	2.7	4.2	0.23	0.51	35.40	21.10	0.21	0.29	38.90	0.02	2.40	0.90	1.90
70	35/774	1335/5	2.4	5.9	2.7	0.31	0.18	61.80	22.30	0.00	0.26	7.60	0.01	2.00	0.52	2.30
71	39/295	1370/1/1	4.3	6.7	5.0	0.20	0.12	43.10	18.30	13.90	0.77	5.40	0.16	0.75	14.20	0.97
72	39/296	1370/1/2	3.3	16.9	4.5	0.25	0.24	55.90	22.30	0.59	1.41	10.10	0.03	0.55	3.20	1.30
73	39/297	1373/1/1	2.1	6.9	6.8	0.17	0.10	60.70	30.20	0.15	0.19	2.20	0.01	0.73	0.69	1.30
74	39/298	1374/1/1	2.5	2.9	4.0	0.40	0.41	65.50	14.80	1.00	0.15	8.60	0.03	0.79	2.30	2.10
75	39/299	1374/2/1	1.9	1.9	4.0	0.36	0.48	24.50	4.00	25.40	0.05	17.80	0.36	0.20	26.80	0.33
76	39/300	1374/2/2	1.6	16.0	2.9	0.81	0.06	2.10	0.92	19.90	0.06	0.60	0.69	0.08	72.20	0.02
77	39/301	1374/2/3	2.3	0.9	4.7	0.31	1.20	46.50	7.90	11.10	0.08	24.60	0.12	0.27	7.90	0.18
78	39/302	1374/2/4	1.8	7.6	4.8	0.20	0.31	46.80	28.80	1.40	2.48	8.20	0.02	0.91	5.30	1.10
79	39/304	1375/2/2	3.1	1.0	2.9	0.24	0.61	21.10	6.20	24.00	0.07	24.30	0.17	0.27	22.10	0.21
80	39/306	1375/2/4	2.4	1.3	4.2	0.20	1.20	53.40	15.00	7.50	0.03	11.70	0.07	0.36	7.50	0.24
81	39/308	1375/2/6	2.0	3.6	5.5	0.13	0.54	51.40	28.00	0.57	3.00	3.20	0.02	0.22	5.70	0.16
82	39/309	1375/2/7	1.7	12.0	5.4	0.19	0.16	54.10	29.00	0.08	2.14	3.70	0.01	0.79	3.40	1.20
83	39/310	1375/3/8	2.8	3.3	2.7	0.21	0.36	63.20	8.40	0.07	1.83	22.50	0.01	0.38	0.97	0.98
84	39/311	1375/3/9	3.3	0.5	2.1	0.44	1.30	26.20	8.50	2.70	0.40	55.70	0.16	0.67	2.50	0.28
85	39/312	1375/3/10	2.7	4.1	2.3	0.19	0.41	34.50	24.70	0.26	7.36	13.50	0.01	1.20	10.60	1.10
86	39/313	1377/2/1	5.9	0.7	1.8	0.82	0.47	24.20	9.70	0.52	0.13	58.80	0.04	0.62	1.60	1.00
87	39/314	1377/2/2	5.0	4.2	3.1	0.16	0.20	22.20	17.60	0.21	4.53	39.60	0.02	0.51	6.90	0.64
88	39/403	1377/1/1	4.5	7.4	7.5	0.04	0.08	5.10	4.60	0.88	0.94	85.70	0.01	0.04	1.30	0.04
89	39/404	1377/1/2	5.3	1.0	3.6	0.17	0.19	15.50	7.30	1.30	0.16	73.00	0.04	0.39	1.40	0.13
90	39/405	1377/1/3	5.5	3.1	3.0	0.16	0.19	41.90	26.00	0.15	1.60	18.80	0.01	2.70	2.60	0.51
91	39/406	1377/1/4	3.4	49.0	4.0	0.54	0.10	48.60	22.70	0.12	0.60	15.60	0.01	1.70	0.83	3.60
92	39/320	1378/1/1	2.2	6.6	3.7	0.22	0.36	43.20	36.90	0.00	1.37	0.34	0.01	6.10	2.10	0.53
93	39/321	1378/1/2	2.7	2.4	4.2	0.16	0.62	38.80	36.10	0.55	0.97	11.60	0.02	1.90	3.00	0.48
94	39/322	1378/1/3	2.7	15.6	3.8	0.66	0.18	43.30	33.90	0.00	3.05	1.50	0.00	2.10	3.80	3.90
95	39/323	1378/2/1	2.1	9.8	3.7	0.23	0.29	42.10	39.80	0.00	1.63	1.90	0.01	2.20	1.70	1.10
96	39/324	1378/3/1	6.4	8.2	1.5	0.45	0.14	59.00	23.60	0.03	0.43	5.50	0.01	1.00	0.47	3.40
97	39/325	1378/3/2	6.3	1.0	1.9	0.12	0.22	17.10	11.80	0.00	0.27	64.80	0.02	1.20	0.82	0.30
98	39/326	1378/3/3	3.1	51.2	1.3	0.87	0.14	54.00	29.70	0.00	0.13	1.60	0.01	1.60	0.09	4.30
99	39/327	1378/3/4	4.1	5.7	3.7	0.20	0.12	36.50	28.30	0.00	0.21	27.20	0.01	0.42	0.42	0.95
100	39/336	1379/1/1	3.7	2.0	4.5	0.14	0.41	35.10	14.60	0.00	0.16	43.50	0.03	1.70	1.50	0.62
101	39/338	1379/1/3	4.1	6.3	4.5	0.19	0.22	52.10	18.30	0.10	3.23	12.70	0.01	1.60	5.20	1.00
102	39/332	1379/3/2	5.5	1.4	2.2	0.21	0.06	12.90	9.10	0.36	0.24	72.40	0.03	0.36	0.88	1.00
103	39/333	1379/3/3	4.9	7.3	2.6	0.46	0.14	40.20	30.90	0.20	3.03	7.00	0.01	2.20	5.90	3.30
104	39/328	1381/1/1	3.5	5.9	4.0	0.28	0.30	33.30	23.80	0.69	2.57	23.60	0.01	1.90	4.40	2.20
105	39/329	1381/1/2	3.7	13.2	3.1	0.33	0.18	47.00	35.50	0.28	0.46	3.60	0.00	2.60	0.76	1.90
106	39/330	1381/1/3	3.4	22.4	2.7	0.48	0.15	44.20	34.70	0.00	1.86	3.10	0.01	1.60	2.70	3.40
107	39/415	1382/2/1	2.8	3.9	3.9	0.29	0.48	43.90	29.90	0.49	1.80	9.10	0.01	0.72	3.10	3.10
108	39/417	1382/2/3	3.8	16.2	3.8	0.67	0.17	46.00	35.70	0.02	0.59	2.60	0.00	1.90	0.27	4.40
109	39/410	1384/1/1	5.4	2.2	0.8	0.24	1.16	68.20	14.70	0.00	0.13	9.20	0.01	1.03	0.34	1.16
110	39/411	1384/1/2	5.2	9.5	0.7	0.12	0.11	76.00	10.70	0.00	0.28	3.50	0.00	2.30	0.31	0.81
111	39/315	1385/2/1	5.2	7.3	4.5	0.25	0.12	21.20	12.60	0.68	0.07	61.30	0.02	0.60	0.51	1.20
112	39/316	1385/2/2	6.1	2.2	1.8	0.10	0.13	26.00	16.00	0.00	0.08	52.50	0.00	1.00	0.65	0.18
113	39/317	1385/2/3	8.0	0.2	0.5	0.99	0.82	44.90	23.00	0.03	0.15	14.90	0.03	1.10	3.70	1.20
114	39/318	1385/2/4	6.8	3.1	0.5	0.35	0.29	46.80	34.50	0.75	0.67	3.70	0.01	2.00	1.70	1.60
115	39/319	1385/2/5	6.2	12.6	1.0	0.21	0.16	64.30	19.70	0.00	1.32	1.20	0.00	2.70	1.70	1.70
116	39/407	1386/1/1	4.3	28.1	1.8	0.37	0.11	44.60	37.60	0.00	1.30	0.92	0.00	2.00	1.50	2.40
117	39/408	1386/1/2	5.2	12.7	2.0	0.74	0.17	46.00	35.70	0.00	0.88	0.68	0.00	3.50	1.40	4.10
118	39/409	1386/1/3	4.5	3.6	2.6	0.21	0.42	43.80	37.30	0.25	1.00	4.00	0.00	1.70	1.50	0.82

Table A2.5 continued.

	Sample	A%	Qtz	Kaolin.	Illite	Rutile	Sid.	Cal.	Crand.	Pyrite	MM/A
1	26/060	4.5	33.0	22.8	6.7	0.8	25.9	0.0	0.3	10.5	1.12
2	26/067	7.4	44.1	11.8	9.0	0.7	27.6	0.0	0.5	6.3	1.11
3	26/069	1.5	22.0	28.8	4.0	0.9	23.6	1.2	0.1	19.3	1.11
4	26/142	7.6	53.5	17.3	10.7	1.4	16.9	0.1	0.1	0.0	1.07
5	26/148	23.6	46.9	17.7	29.6	1.0	4.8	0.0	0.1	0.0	1.05
6	26/163	6.9	68.3	12.8	13.6	1.2	3.7	0.4	0.1	0.0	1.02
7	26/172	7.0	65.2	23.7	5.7	1.0	4.1	0.3	0.1	0.0	1.03
8	26/175	6.8	46.6	23.9	18.6	1.0	5.5	3.4	1.1	0.0	1.10
9	26/186	6.0	33.1	15.4	4.8	0.4	34.6	3.2	0.7	7.8	1.17
10	26/255	6.2	42.9	17.8	31.6	1.3	4.3	0.3	1.9	0.0	1.03
11	26/259	5.3	30.2	26.6	31.7	1.1	4.3	0.5	5.5	0.0	1.04
12	26/263	5.2	25.2	12.2	18.3	0.8	35.9	0.0	7.6	0.0	1.14
13	26/267	3.4	14.2	38.3	16.7	1.4	11.6	1.7	16.1	0.0	1.08
14	26/278	4.5	44.6	37.3	9.1	3.3	5.4	0.0	0.4	0.0	1.02
15	26/281	6.0	46.9	28.5	18.6	2.5	3.4	0.0	0.2	0.0	1.02
16	26/289	2.8	36.0	33.6	16.6	2.0	8.0	2.6	1.2	0.0	1.02
17	26/298	3.3	16.7	13.0	8.5	0.9	59.4	0.0	1.5	0.0	1.20
18	26/340	5.5	47.7	16.2	20.8	2.0	9.6	0.0	0.4	3.4	1.07
19	26/343	6.2	66.1	22.8	4.7	1.5	2.4	0.6	0.5	1.5	1.05
20	26/350	6.5	62.9	17.0	13.8	1.5	2.8	0.6	0.3	1.1	1.05
21	26/358	7.1	63.3	14.3	15.1	1.3	2.6	0.6	0.2	2.5	1.04
22	26/376	3.2	29.0	25.3	19.0	1.2	24.1	0.0	1.3	0.0	1.11
23	26/454	7.2	43.7	40.1	7.5	3.3	2.7	0.0	2.0	0.5	1.07
24	26/457	5.3	36.6	41.8	15.8	1.5	0.0	1.8	0.6	1.8	1.07
25	26/462	6.5	36.3	19.6	27.2	1.5	1.6	1.5	10.9	1.4	1.08
26	26/467	4.4	26.1	32.2	24.9	1.3	6.4	1.7	5.0	2.4	1.10
27	26/537	6.8	38.5	20.5	27.7	1.0	12.0	0.0	0.4	0.0	1.08
28	26/547	6.7	23.5	24.5	35.5	1.0	6.7	0.4	8.3	0.0	1.09
29	26/565	3.9	19.4	16.6	19.1	0.8	42.4	1.0	0.6	0.0	1.18
30	26/576	7.0	20.0	32.4	36.9	1.3	4.3	0.6	4.6	0.0	1.09
31	26/595	2.0	31.9	19.6	11.1	1.0	34.4	0.0	2.0	0.0	1.13
32	26/645	3.7	8.8	12.1	6.2	0.4	71.6	0.0	1.0	0.0	1.30
33	26/646	3.5	2.5	7.6	1.2	0.2	88.3	0.0	0.1	0.0	1.39
34	26/662	5.8	57.3	21.3	3.8	1.0	10.1	0.8	0.2	5.6	1.06
35	26/671	7.0	55.6	24.6	11.5	1.1	6.8	0.0	0.4	0.0	1.03
36	26/677	7.1	43.7	31.0	20.0	2.0	3.0	0.0	0.2	0.0	1.05
37	26/687	6.5	43.5	24.6	25.9	1.4	3.6	0.1	0.9	0.0	1.04
38	26/691	5.5	52.9	18.1	19.2	1.3	3.6	0.4	0.5	3.9	1.04
39	26/695	7.0	18.4	7.4	8.3	0.4	50.9	2.1	0.8	11.7	1.17
40	26/842	4.8	59.8	18.7	14.2	2.6	3.9	0.5	0.2	0.0	0.96
41	26/851	5.5	63.9	20.8	10.6	1.7	2.5	0.4	0.2	0.0	0.97
42	26/860	1.9	33.8	35.3	14.6	1.6	11.5	1.7	1.5	0.0	0.88
43	29/652	5.9	51.0	26.5	10.8	3.1	6.5	0.6	0.1	1.5	1.07
44	29/655	6.0	50.2	26.8	16.7	2.3	0.0	1.8	0.1	2.0	1.06
45	29/659	5.1	36.6	24.0	32.3	1.6	0.0	2.6	0.3	2.8	1.07
46	29/664	2.7	26.2	18.9	8.8	1.1	35.1	9.4	0.3	0.0	1.12
47	29/153	5.9	61.3	18.3	9.6	1.3	5.0	0.9	0.3	3.2	1.05
48	29/100	4.9	33.6	23.6	29.7	1.4	6.6	0.0	4.0	1.1	1.08
49	29/106	5.1	29.8	27.2	35.1	1.4	4.9	0.0	0.3	1.3	1.08
50	29/200	6.7	51.0	29.0	11.9	2.7	4.7	0.2	0.1	0.3	1.07
51	26/959	5.9	55.9	23.7	12.2	3.2	1.3	0.7	0.3	2.7	1.05
52	26/952	6.2	39.9	16.9	34.1	1.6	5.8	0.3	1.4	0.0	1.06
53	26/979	4.1	34.0	20.8	2.7	1.1	26.2	15.0	0.1	0.0	1.14
54	26/984	6.2	45.3	26.3	20.3	1.3	4.0	1.9	0.8	0.0	1.05
55	26/995	3.4	46.1	31.9	13.4	1.3	4.0	2.5	0.8	0.0	1.05
56	29/001	4.7	18.5	13.0	11.5	0.6	55.0	0.0	1.3	0.0	1.22
57	29/016	4.1	27.3	31.3	26.9	1.9	10.3	0.4	1.9	0.0	1.09
58	29/075	5.6	33.6	30.5	25.1	2.1	5.5	0.9	2.2	0.0	1.07
59	29/037	5.9	40.0	31.7	4.9	2.1	17.2	0.0	0.1	4.1	1.10
60	29/040	7.4	54.3	27.8	5.5	2.5	4.9	1.4	0.1	3.5	1.05

Table A2.6 Calculated mineral assemblages, base 100%, for drillhole samples of Paparoa coal from the Rapahoe Sector, Greymouth Coalfield. For drillhole numbers see Table A2.3.

A= ash%, air dried basis Qtz=quartz Kaolin=kaolinite Sid=siderite Cal=calcite Crand=crandallite

Sample	A%	Qtz	Kaolin.	Illite	Rutile	Sid.	Cal.	Crand.	Pyrite	MM/A
61 29/046	4.8	34.6	30.7	25.1	1.5	7.9	0.2	0.1	0.0	1.07
62 29/047	6.5	59.3	22.3	13.6	1.6	2.0	0.4	0.0	0.8	1.05
63 29/053	6.0	35.3	25.6	31.5	1.6	5.9	0.1	0.1	0.0	1.08
64 29/061	3.5	38.0	18.8	22.9	1.2	0.0	4.2	3.4	11.6	1.10
65 29/026	1.7	37.8	32.0	18.9	1.5	7.6	1.8	0.4	0.0	1.07
66 29/033	3.4	26.5	20.5	3.7	1.0	48.1	0.0	0.2	0.0	1.20
67 29/674	6.0	65.5	22.0	1.6	1.5	0.0	2.4	1.0	6.1	1.06
68 29/685	2.9	40.3	20.6	7.7	1.0	15.4	7.5	0.2	7.3	1.08
69 29/696	6.6	67.7	19.9	5.3	1.4	0.0	1.7	0.1	3.9	1.04
70 29/711	6.1	38.3	13.7	7.0	0.8	5.7	0.9	0.2	33.5	0.99
71 29/230	4.5	59.6	27.3	4.7	1.7	4.2	1.4	0.3	0.8	1.06
72 29/235	3.6	18.2	10.1	9.3	0.6	61.5	0.0	0.3	0.0	1.25
73 29/245	5.2	30.0	16.6	0.4	1.0	26.4	0.0	2.6	23.0	1.07
74 29/752	1.6	12.5	48.8	21.5	2.4	8.5	0.5	5.9	0.0	0.71
75 29/735	3.6	26.0	19.4	16.8	0.7	36.6	0.0	0.5	0.0	1.00
76 29/754	5.9	31.6	21.5	27.0	0.9	18.0	0.0	0.9	0.0	1.00
77 31/729	5.7	9.5	8.0	4.4	0.3	77.4	0.0	0.4	0.0	1.21
78 31/735	2.9	27.8	25.4	19.1	0.9	21.2	2.0	3.7	0.0	0.92
79 31/736	3.5	51.4	29.4	8.9	1.6	7.4	0.0	0.3	1.0	1.07
80 31/740	6.3	30.9	22.1	11.7	2.5	32.3	0.0	0.4	0.0	1.17
81 31/972	3.2	32.7	31.3	18.3	1.5	14.9	0.0	1.3	0.0	1.11
82 31/779	6.3	14.0	21.5	11.5	0.7	49.4	0.5	2.4	0.0	1.23
83 31/800	2.7	27.9	41.6	20.0	1.5	8.0	0.5	0.5	0.0	1.10
84 31/847	6.7	38.5	32.0	16.7	3.3	4.4	0.5	4.4	0.3	1.08
85 32/008	6.5	36.3	27.2	20.1	3.5	6.9	0.3	5.7	0.0	1.09
86 32/013	4.1	30.9	29.7	15.6	1.3	21.6	0.0	0.9	0.0	1.13
87 34/372	6.5	12.4	16.8	45.0	1.4	16.3	0.0	8.1	0.0	1.13
88 34/370	4.4	15.4	43.9	22.3	1.7	5.1	2.6	9.1	0.0	1.13
89 34/371	5.5	12.2	14.4	21.2	0.6	49.2	0.0	2.4	0.0	1.24
90 34/375	5.0	25.8	24.5	34.7	1.5	5.8	0.5	7.4	0.0	1.10
91 34/374	2.3	17.5	17.4	2.5	0.6	62.0	0.0	0.0	0.0	1.27
92 34/373	5.9	44.2	16.8	23.7	1.2	13.8	0.0	0.4	0.0	1.09
93 35/055	3.9	19.2	13.6	12.4	0.7	53.0	0.0	1.1	0.0	1.24
94 35/057	5.8	21.2	16.4	26.1	0.9	25.5	2.4	7.5	0.0	1.16
95 35/056	4.3	18.6	19.7	6.6	0.9	52.4	0.0	1.8	0.0	1.25
96 35/058	6.2	21.6	13.9	27.9	0.8	31.3	0.0	4.4	0.0	1.17
97 35/059	3.6	22.1	30.2	24.9	1.5	19.6	0.0	1.6	0.0	1.13
98 35/060	3.7	3.9	22.1	14.6	0.5	57.1	0.0	1.8	0.0	1.28
99 35/061	6.2	17.7	15.5	34.7	1.0	23.4	0.0	7.6	0.0	1.14
100 35/062	5.9	30.2	16.7	25.6	0.9	26.2	0.0	0.5	0.0	1.14
101 35/064	5.8	26.5	18.7	22.9	1.4	25.8	0.0	4.7	0.0	1.14
102 35/063	6.5	16.9	16.3	22.9	0.7	39.9	0.0	3.3	0.0	1.20
103 35/231	5.7	26.4	19.6	30.6	0.9	15.2	1.7	5.6	0.0	1.12
104 35/230	2.2	34.7	17.8	6.1	0.7	40.1	0.0	0.7	0.0	1.19

Table A2.6 continued.

	Sample	A%	Qtz	Kaolin.	Illite	Boehm.	Rutile	Dol.	Cal.	Crand.	Pyrite	MM/A
1	31/050	0.4	5.8	45.3	11.2	0.0	0.9	1.5	2.5	1.7	31.0	1.21
2	31/051	1.9	0.0	84.2	2.5	4.4	0.2	0.6	1.1	0.6	6.6	1.15
3	31/056	31.4	0.0	56.4	33.2	3.5	1.5	1.4	0.0	0.4	3.6	1.13
4	31/057	3.5	0.0	65.8	13.7	6.5	1.8	1.3	0.0	0.3	10.5	1.16
5	31/058	1.3	0.0	82.7	4.1	4.0	2.3	0.8	1.4	0.2	4.4	1.15
6	31/061	7.6	0.0	47.4	35.5	0.0	1.3	1.6	0.0	0.7	13.4	1.15
7	31/062	0.4	0.0	43.7	18.4	6.7	1.4	1.2	3.3	0.3	24.8	1.19
8	31/063	4.0	0.0	50.6	36.7	3.5	2.7	0.9	0.3	0.4	4.9	1.13
9	31/064	0.4	0.0	51.7	6.8	4.6	1.2	2.0	2.9	1.1	29.7	1.22
10	31/065	3.6	0.0	76.3	6.4	2.8	1.4	0.6	2.9	2.5	7.1	1.16
11	31/059	1.2	0.0	64.9	24.3	3.1	1.9	1.3	1.1	0.5	3.0	1.13
12	31/060	0.5	0.0	58.5	30.9	1.3	1.3	1.2	3.3	0.4	3.1	1.11
13	31/086	0.3	0.0	30.9	10.5	0.5	0.8	0.6	2.5	0.4	53.9	1.27
14	31/087	1.4	0.0	77.8	9.1	3.0	0.8	0.3	1.2	0.1	7.7	1.15
15	31/044	0.9	0.0	37.5	6.9	6.6	2.0	0.9	4.2	0.3	41.7	1.25
16	31/045	11.1	0.0	48.0	41.0	2.5	2.4	2.2	0.0	1.4	2.5	1.12
17	31/046	11.4	0.0	47.8	43.2	4.0	2.1	1.1	0.2	0.4	1.2	1.11
18	31/047	3.7	0.0	47.6	39.9	5.0	3.6	1.3	0.2	0.6	1.7	1.12
19	31/048	1.1	0.0	52.7	41.2	1.4	0.9	0.8	1.5	0.1	1.4	1.11
20	31/049	18.6	0.0	63.8	29.3	0.0	2.1	1.2	0.0	0.8	2.6	1.12
21	31/040	4.0	0.0	59.4	26.3	5.0	1.9	2.3	0.3	0.7	4.1	1.13
22	31/041	0.5	1.8	55.8	21.4	0.0	1.2	0.9	3.0	0.3	15.7	1.16
23	31/113	6.5	37.4	11.7	41.9	0.0	0.9	1.2	0.0	0.2	6.7	1.07
24	31/114	2.6	30.8	46.3	13.2	0.0	0.5	0.6	0.6	1.0	7.0	1.10
25	31/069	0.2	9.8	39.5	9.8	0.0	1.2	1.3	5.5	0.2	32.7	1.19
26	31/070	2.4	0.0	81.1	4.3	3.5	0.5	0.7	1.8	1.1	7.0	1.16
27	31/083	4.6	1.1	54.9	27.1	0.0	1.4	1.4	0.0	0.5	13.5	1.16
28	31/084	0.3	13.7	50.4	24.3	0.0	1.1	1.6	1.5	0.2	7.1	1.12
29	31/085	4.8	0.0	60.9	27.0	1.9	1.8	0.9	0.0	0.3	7.3	1.14
30	31/075	4.0	4.5	68.4	18.6	0.0	1.2	1.3	0.1	1.4	4.6	1.13
31	31/076	0.1	1.4	65.9	12.1	0.0	1.0	1.6	3.3	0.3	14.5	1.15
32	31/077	0.5	0.0	49.1	12.7	22.2	0.8	1.1	0.6	3.6	9.9	1.17
33	31/078	0.3	0.0	55.5	9.7	14.9	1.5	1.1	4.2	4.9	8.3	1.16
34	31/079	0.1	0.0	47.4	10.9	19.1	2.0	0.7	5.1	6.3	8.4	1.15
35	31/080	0.3	0.6	51.2	7.4	0.0	1.1	0.7	2.5	1.0	35.6	1.22
36	31/081	1.2	0.0	56.8	4.8	5.7	0.5	0.4	0.5	1.9	29.4	1.21
37	31/082	3.8	0.0	80.6	3.8	0.0	0.5	0.5	7.6	5.1	1.9	1.17
38	31/088	33.5	0.0	56.8	35.4	2.1	1.5	1.4	0.0	0.4	2.5	1.12
39	31/089	1.6	2.8	74.6	11.9	0.0	1.3	1.3	0.9	0.2	7.1	1.14
40	31/090	0.9	1.0	42.7	12.9	0.0	1.1	0.5	0.8	0.4	40.6	1.24
41	31/071	36.3	0.0	55.9	31.5	7.1	1.4	1.3	0.0	0.5	2.3	1.13
42	31/072	2.0	1.0	88.0	3.7	0.0	0.3	0.5	0.4	0.1	6.0	1.15
43	31/073	0.5	3.3	31.4	3.9	0.0	0.6	0.5	1.1	0.1	59.2	1.30
44	31/074	1.8	1.3	14.3	0.9	0.0	0.2	0.3	0.9	0.0	82.0	1.40
45	31/106	2.6	1.1	65.6	12.8	0.0	1.1	0.9	0.2	0.4	18.0	1.17
46	31/107	13.5	1.7	59.8	27.2	0.0	2.3	1.2	0.1	0.2	7.5	1.13
47	31/095	4.7	0.0	61.9	16.9	1.7	1.5	0.8	0.8	0.7	15.8	1.17
48	31/109	2.8	0.0	42.6	18.0	11.6	0.5	0.5	0.6	0.2	25.8	1.20
49	31/103	2.1	1.5	46.9	36.3	0.0	1.7	1.3	0.1	1.1	11.1	1.14
50	31/104	0.4	0.0	27.8	31.3	3.2	0.8	1.4	2.2	0.5	32.8	1.20
51	31/105	1.5	0.0	21.7	44.3	8.5	0.5	1.1	0.3	1.5	22.1	1.17
52	31/110	1.6	0.0	8.5	12.4	4.4	0.3	2.5	2.3	0.6	69.0	1.33
53	31/111	0.4	10.4	6.1	16.1	0.0	0.4	1.2	3.6	0.2	61.9	1.29
54	31/112	2.8	3.9	9.5	27.4	0.0	0.2	0.5	0.7	0.2	57.6	1.29
55	31/039	0.5	0.0	50.5	19.0	5.2	0.4	1.9	2.0	0.0	21.2	1.18

Table A2.7 Calculated mineral assemblages, base 100%, for drillhole samples of Brunner coal from Webb/Baynes, Buller Coalfield. For drillhole numbers see Table A2.4.

Mineral abbreviations: See Table A2.6

	Sample	A%	Qtz	Kaolin.	Illite	Boehm.	Rutile	Dol.	Cal.	Crand.	Pyrite	MM/A
56	31/052	21.4	0.9	55.8	35.4	0.0	1.6	1.7	0.0	0.7	3.9	1.13
57	31/053	1.9	0.0	69.2	17.2	2.8	2.0	1.1	1.7	0.6	5.4	1.14
58	31/054	0.5	0.0	71.1	13.2	2.4	1.8	1.0	3.8	0.2	6.5	1.14
59	31/055	6.9	0.0	67.7	20.7	3.1	2.7	1.2	0.7	0.8	3.1	1.13
60	31/043	1.5	0.0	72.6	3.2	2.2	1.1	0.3	1.7	0.1	18.7	1.18
61	31/066	13.4	0.1	54.6	33.5	0.0	1.7	1.7	0.0	0.5	7.7	1.13
62	31/067	0.3	0.0	45.9	10.0	5.9	0.9	1.3	2.7	0.7	32.6	1.22
63	31/068	2.7	0.0	71.8	12.1	2.5	1.7	0.9	2.7	0.6	7.8	1.15
64	31/031	1.7	1.8	39.7	19.7	0.0	2.7	1.0	3.0	1.8	30.3	1.21
65	31/032	0.2	5.3	29.5	14.4	0.0	1.9	1.2	5.9	0.0	41.8	1.20
66	31/216	1.2	0.0	32.5	10.2	39.0	0.8	9.7	0.6	0.5	6.6	1.13
67	31/108	1.5	0.0	8.6	20.7	26.8	0.5	4.5	0.7	0.4	37.9	1.21
68	31/042	0.4	0.3	49.6	19.9	0.0	1.1	1.4	3.4	0.2	24.2	1.18
69	31/094	0.2	0.0	48.0	16.4	13.1	1.2	0.7	5.0	2.6	13.0	1.16
70	31/134	10.5	0.0	50.6	38.6	4.3	2.0	1.6	0.0	0.4	2.5	1.12
71	31/033	14.1	0.0	43.6	35.5	14.9	1.7	1.7	0.0	0.8	1.7	1.13
72	31/034	2.9	0.0	56.4	8.7	21.5	1.8	0.4	1.9	1.2	8.1	1.16
73	31/130	5.6	31.3	25.9	33.4	0.0	1.4	1.4	0.0	0.3	6.4	1.09
74	31/131	0.6	37.3	20.2	31.2	0.0	1.0	1.1	1.7	0.1	7.4	1.07
75	31/132	2.3	62.6	0.8	29.2	0.0	0.5	0.7	0.1	0.7	5.4	1.04
76	31/133	1.1	46.0	17.7	20.6	0.0	0.9	0.7	1.5	0.2	12.5	1.08
77	31/116	11.8	1.5	43.2	31.1	0.0	1.0	1.1	0.0	0.3	21.8	1.17
78	31/117	1.0	0.9	47.1	4.6	0.0	2.6	0.2	1.2	0.2	43.2	1.26
79	31/118	0.4	2.9	24.6	6.3	0.0	0.7	0.3	1.8	0.1	63.1	1.31
80	31/119	2.6	Jarosite present, minerals not calculated									1.21
81	31/120	0.3	''			''		''				1.04
82	31/121	1.7	3.2	14.6	17.1	0.0	0.3	0.3	1.0	0.1	63.3	1.30
83	31/099	1.4	8.9	7.0	11.1	0.0	0.4	0.6	0.5	0.3	71.2	1.34
84	31/100	0.2	9.9	33.7	31.0	0.0	0.9	3.1	5.4	0.3	15.6	1.13
85	31/091	0.2	6.7	46.8	20.4	0.0	1.3	3.7	3.0	1.6	16.6	1.16
86	31/092	0.2	0.0	34.5	18.9	2.2	1.0	6.0	1.9	1.0	34.6	1.23
87	31/093	0.4	0.0	42.3	19.9	7.2	0.9	2.7	2.2	0.4	24.4	1.16
88	31/143	1.0	3.2	56.9	17.3	0.0	0.8	0.8	0.7	0.6	19.6	1.18
89	31/144	1.4	29.1	15.8	43.6	0.0	0.9	2.5	0.0	0.6	7.5	1.09
90	31/145	0.8	19.6	29.6	38.1	0.0	1.0	2.4	0.4	0.9	8.1	1.11
91	31/146	2.4	12.0	54.3	25.9	0.0	0.5	1.6	0.1	0.3	5.2	1.12
92	31/096	8.5	0.1	64.5	25.0	0.0	2.3	1.0	0.0	0.6	6.3	1.14
93	31/097	0.3	2.5	28.8	6.7	0.0	0.9	0.6	3.3	0.1	57.1	1.29
94	31/098	0.1	5.3	49.0	23.0	0.0	2.0	2.0	6.6	0.3	11.9	1.14
95	31/970	0.2	3.3	32.8	7.1	0.0	0.7	0.5	2.0	0.3	53.3	1.28
96	31/971	3.0	8.5	50.7	7.2	0.0	0.5	0.4	0.8	0.2	31.7	1.21
97	31/135	5.6	1.1	70.9	21.7	0.0	2.3	0.9	0.0	0.5	2.5	1.13
98	31/136	0.7	3.1	45.0	10.5	0.0	0.8	0.9	0.7	0.2	38.8	1.24
99	31/137	3.2	0.3	47.8	3.1	0.0	0.3	0.2	0.3	0.1	48.0	1.28
100	31/122	4.7	0.0	62.5	30.2	0.8	1.2	1.4	0.0	0.5	3.5	1.13
101	31/123	0.6	4.7	39.4	25.1	0.0	1.3	1.6	0.8	0.3	26.8	1.19
102	31/124	2.1	3.9	30.6	16.8	0.0	0.8	0.9	0.4	0.6	45.8	1.25
103	31/115	0.3	31.1	17.3	12.7	0.0	0.7	0.9	1.5	0.2	35.6	1.18
104	31/138	2.0	20.3	29.5	20.8	0.0	0.9	1.4	0.0	0.5	26.6	1.17
105	31/147	3.5	51.1	6.6	34.6	0.0	0.6	1.0	0.4	0.5	5.3	1.06
106	31/148	0.7	48.0	9.0	28.3	0.0	0.8	0.8	1.1	0.4	11.6	1.08
107	31/149	4.0	0.0	63.2	10.1	0.0	0.3	0.3	0.6	0.2	25.3	1.20
108	31/968	2.2	2.0	15.2	14.9	0.0	0.7	0.7	0.5	0.3	65.7	1.32
109	31/969	0.3	0.0	48.6	13.8	3.1	1.1	0.7	3.8	4.1	24.9	1.19
110	31/128	2.7	0.0	39.2	21.4	16.8	3.1	7.9	6.0	0.6	4.9	1.12
111	31/129	1.5	1.1	45.6	31.4	0.0	1.0	2.7	2.7	0.3	15.2	1.15
112	31/101	0.8	8.9	17.9	7.5	0.0	0.6	0.5	0.9	0.1	63.6	1.31
113	31/102	14.8	0.0	48.7	35.9	0.2	1.6	1.3	0.3	0.6	11.5	1.14
114	31/141	1.1	5.0	21.2	5.3	0.0	0.3	1.0	0.6	0.2	66.5	1.31
115	31/142	5.0	0.0	62.9	13.3	0.2	0.8	0.3	0.6	0.7	21.1	1.19
116	31/140	5.2	27.8	37.8	15.6	0.0	0.8	0.6	0.5	0.8	16.2	1.13

Table A2.7 continued.

	Sample	A%	Qtz	Kaolin.	Illite	Boehm.	Rutile	Dol.	Cal.	Crand.	Pyrite	MM/A
1	32/596	2.1	18.0	61.9	12.4	0.0	1.3	1.5	0.4	0.4	4.0	1.11
2	32/528	2.2	13.6	35.8	9.6	0.0	1.7	0.7	0.5	0.8	37.3	1.21
3	32/529	14.5	27.8	17.0	44.6	0.0	2.4	2.9	0.0	2.1	3.3	1.08
4	32/525	0.6	6.6	35.5	3.5	0.0	0.3	0.8	1.4	0.4	51.4	1.28
5	32/526	19.8	2.1	48.4	43.4	0.0	2.1	1.7	0.0	0.5	1.8	1.11
6	32/527	10.7	2.6	46.8	42.9	0.0	2.1	1.8	0.0	0.5	3.3	1.12
7	32/244	13.3	0.0	49.7	38.3	3.4	2.4	3.2	0.0	0.0	2.9	1.12
8	32/597	3.8	14.0	9.6	24.0	0.0	0.5	1.1	0.2	0.3	50.3	1.24
9	32/521	0.6	23.0	37.8	25.1	0.0	1.2	3.2	1.0	0.8	7.9	1.11
10	32/192	3.5	3.8	69.6	8.6	0.0	5.2	1.4	3.9	5.0	2.5	1.14
11	32/522	1.8	18.0	23.0	12.5	0.0	0.7	1.7	1.3	1.7	41.1	1.22
12	32/523	8.2	12.0	40.8	16.7	0.0	2.8	1.3	9.4	14.6	2.4	1.16
13	32/524	1.9	40.1	33.7	6.4	0.0	1.5	1.2	4.2	2.5	10.5	1.11
14	32/301	7.2	42.1	6.6	16.3	0.0	0.5	3.3	0.0	0.3	31.0	1.15
15	32/598	1.0	18.2	19.1	3.2	0.0	0.7	1.4	0.1	0.1	57.2	1.27
16	32/306	5.7	38.6	25.9	18.8	0.0	3.9	1.4	0.6	1.7	9.1	1.09
17	32/599	6.3	0.0	36.2	29.5	3.8	2.3	1.0	0.0	0.8	26.4	1.19
18	32/600	2.1	6.1	7.0	4.8	0.0	0.3	0.8	1.1	0.0	79.9	1.33
19	32/395	0.8	6.2	3.1	1.8	0.0	0.3	0.5	0.0	10.1	78.9	1.36
20	32/394	4.0	9.8	35.7	17.7	0.0	2.0	1.6	12.8	17.5	3.0	1.18
21	32/386	5.1	3.7	59.3	7.8	0.0	3.4	0.9	3.1	4.3	17.5	1.19
22	35/752	5.5	0.7	1.9	0.2	0.0	0.0	0.0	0.1	0.2	96.8	1.47
23	35/753	0.6	14.4	47.5	1.4	0.0	0.5	0.5	1.4	0.2	34.2	1.21
24	35/754	6.0	14.0	53.9	23.0	0.0	4.9	1.5	0.0	0.5	2.1	1.11
25	35/327	3.1	4.6	20.2	0.8	0.0	0.1	0.8	0.0	0.3	73.3	1.36
26	35/328	0.7	4.1	13.8	1.4	0.0	0.4	0.6	0.7	0.6	78.3	1.38
27	35/329	0.4	24.3	16.7	1.9	0.0	0.5	1.3	0.6	0.6	54.2	1.26
28	35/330	1.8	39.4	50.0	0.7	0.0	1.0	0.4	0.8	0.7	7.1	1.10
29	35/759	31.9	0.0	51.2	31.7	6.1	1.4	1.9	0.1	0.0	7.5	1.14
30	35/760	34.3	0.0	56.0	29.6	2.9	1.7	1.8	0.0	0.0	8.0	1.14
31	35/761	19.2	1.1	58.5	21.0	0.0	1.9	1.6	2.3	5.0	8.6	1.16
32	35/482	0.8	28.9	57.7	5.4	0.0	2.2	0.9	0.8	0.3	4.0	1.10
33	35/762	11.8	2.9	45.5	14.8	0.0	1.2	0.8	7.9	10.3	16.6	1.21
34	35/763	1.5	8.5	10.1	4.1	0.0	0.3	0.1	1.1	0.4	75.5	1.35
35	35/764	0.7	5.8	14.4	3.9	0.0	0.4	0.4	1.1	0.4	73.6	1.35
36	35/765	0.4	10.0	53.8	1.9	0.0	1.6	0.0	1.7	0.3	30.6	1.21
37	35/766	4.0	43.9	43.8	5.6	0.0	2.8	0.6	0.5	1.5	1.2	1.08
38	35/484	2.0	13.0	68.7	6.9	0.0	2.8	1.0	2.1	3.2	2.4	1.13
39	35/485	0.4	0.0	84.2	2.1	1.2	0.4	0.9	3.6	0.6	7.1	1.17
40	35/486	3.8	0.0	85.9	0.5	0.5	0.2	0.0	5.9	5.9	1.0	1.17
41	35/487	33.4	0.0	60.7	31.9	3.3	1.4	1.0	0.0	0.0	1.8	1.12
42	35/488	4.6	0.0	75.2	12.0	6.1	1.5	0.9	0.6	1.9	1.8	1.14
43	35/489	0.6	1.3	89.6	2.3	0.0	1.2	0.5	1.4	0.3	3.4	1.15
44	35/490	4.5	19.3	49.5	14.8	0.0	2.0	0.7	5.4	6.4	1.9	1.13
45	35/305	4.0	5.5	1.6	9.8	0.0	0.2	0.5	0.1	0.6	81.7	1.39
46	35/306	3.4	5.2	25.0	3.8	0.0	1.7	0.1	1.9	1.5	60.8	1.31
47	35/307	14.4	23.3	30.1	12.1	0.0	2.9	1.0	0.8	1.9	27.9	1.17
48	35/308	0.9	18.0	25.7	18.7	0.0	0.6	1.5	0.5	0.5	34.5	1.19
49	35/309	0.1	14.2	27.9	11.7	0.0	1.0	4.4	9.8	1.2	29.8	1.23
50	35/313	14.5	19.8	15.6	36.2	0.0	1.9	2.3	1.9	4.2	18.2	1.12
51	35/315	4.0	0.5	15.3	50.7	0.0	2.1	1.0	0.0	3.3	27.2	1.17
52	35/316	9.5	2.0	41.7	37.4	0.0	2.1	2.3	1.5	3.7	9.2	1.14
53	35/317	3.2	6.9	10.2	13.7	0.0	0.2	1.4	0.9	0.4	66.2	1.33
54	35/318	1.2	0.0	58.8	7.3	21.4	0.6	4.5	0.0	0.5	7.0	1.17
55	35/319	1.2	0.0	51.4	12.8	22.4	0.6	4.7	0.0	0.4	7.7	1.17
56	35/320	5.2	2.5	38.7	25.7	0.0	2.0	2.6	3.0	5.4	20.0	1.19
57	35/321	3.1	12.3	6.4	47.0	0.0	1.8	2.5	9.0	11.8	9.4	1.16
58	35/483	2.1	3.1	55.2	17.6	0.0	1.9	1.3	0.0	0.4	20.5	1.18
59	35/323	6.4	17.2	13.3	6.6	0.0	0.4	0.8	0.0	0.7	61.0	1.29
60	35/324	1.4	0.0	26.4	3.2	13.6	0.2	1.6	0.0	0.8	54.3	1.31

Table A2.8 Calculated mineral assemblages, base 100%, for drillhole samples of Brunner coal from the Upper Waimangaroa Sector, Buller Coalfield. For drillhole numbers, see Table A2.5.

Mineral abbreviations: See Table A2.6

	Sample	A%	Qtz	Kaolin.	Illite	Boehm.	Rutile	Dol.	Cal.	Crand.	Pyrite	MM/A
61	35/325	0.6	18.9	40.4	2.5	0.0	0.5	4.4	0.0	1.6	31.8	1.21
62	35/326	3.6	41.3	31.1	14.3	0.0	1.5	0.4	0.0	1.2	10.4	1.09
63	35/767	2.6	7.7	12.6	14.4	0.0	1.4	0.9	3.3	6.4	53.3	1.28
64	35/768	6.6	23.0	7.5	7.8	0.0	2.0	0.4	28.6	0.6	30.0	1.08
65	35/769	11.6	5.5	35.7	24.8	0.0	1.9	1.7	10.8	8.5	11.1	1.15
66	35/770	10.4	1.3	7.7	1.2	0.0	0.2	0.6	0.0	1.2	87.8	1.45
67	35/771	2.8	3.6	24.6	3.6	0.0	0.9	0.4	1.6	2.3	62.9	1.33
68	35/772	28.1	8.2	43.6	31.1	0.0	0.8	1.0	0.0	11.4	3.9	1.13
69	35/773	2.7	7.7	23.4	17.2	0.0	2.0	0.9	0.7	0.7	47.5	1.26
70	35/774	5.9	33.0	27.1	24.8	0.0	1.9	1.4	0.0	0.7	11.1	1.10
71	39/295	6.7	22.1	30.1	11.0	0.0	0.8	0.9	24.6	2.3	8.2	1.05
72	39/296	16.9	29.3	32.6	13.9	0.0	0.5	1.1	3.9	4.0	14.6	1.13
73	39/297	6.9	24.6	54.7	14.6	0.0	0.7	0.8	0.7	0.6	3.3	1.10
74	39/298	2.9	45.4	13.3	22.8	0.0	0.8	1.8	2.9	0.4	12.6	1.09
75	39/299	1.9	18.8	5.5	3.5	0.0	0.2	1.6	44.8	0.1	25.6	1.06
76	39/300	16.0	0.8	1.3	0.2	0.0	0.1	2.8	94.2	0.1	0.7	1.38
77	39/301	0.9	34.8	14.5	1.9	0.0	0.3	1.3	12.4	0.2	34.6	1.10
78	39/302	7.6	14.7	45.8	11.9	0.0	0.9	0.9	7.0	7.0	11.9	1.15
79	39/304	1.0	13.1	11.0	2.2	0.0	0.3	1.1	37.1	0.2	35.0	1.07
80	39/306	1.3	35.4	30.4	2.7	0.0	0.4	0.9	12.8	0.1	17.5	1.09
81	39/308	3.6	22.5	53.3	1.8	0.0	0.2	0.6	7.9	8.9	4.9	1.14
82	39/309	12.0	21.7	47.5	13.3	0.0	0.8	0.9	4.1	6.2	5.5	1.13
83	39/310	3.3	49.2	4.8	9.8	0.0	0.3	0.8	0.0	4.8	30.3	1.14
84	39/311	0.5	13.2	12.1	2.5	0.0	0.5	1.6	2.5	0.9	66.7	1.30
85	39/312	4.1	12.8	24.2	11.1	0.0	1.1	0.8	12.1	19.5	18.4	1.21
86	39/313	0.7	9.4	9.4	8.6	0.0	0.5	2.9	0.6	0.3	68.3	1.33
87	39/314	4.2	5.8	18.5	6.0	0.0	0.4	0.6	7.4	11.1	50.1	1.30
88	39/403	7.4	0.6	5.2	0.3	0.0	0.0	0.1	1.1	1.9	90.7	1.44
89	39/404	1.0	5.1	10.6	1.1	0.0	0.3	0.6	1.4	0.3	80.6	1.39
90	39/405	3.1	12.1	45.5	5.3	0.0	2.5	0.7	2.9	4.4	26.5	1.19
91	39/406	49.0	18.7	15.8	38.0	0.0	1.6	2.1	0.0	1.7	22.2	1.14
92	39/320	6.6	1.1	77.7	6.3	0.0	6.5	1.1	2.4	4.3	0.5	1.13
93	39/321	2.4	0.0	65.5	5.2	2.7	1.9	0.7	4.2	2.8	17.0	1.18
94	39/322	15.6	4.2	32.8	43.6	0.0	2.1	3.0	3.0	8.9	2.3	1.12
95	39/323	9.8	0.0	70.5	12.9	3.7	2.3	1.1	1.4	5.0	3.0	1.14
96	39/324	8.2	29.2	20.8	38.0	0.0	1.0	1.5	0.0	1.3	8.3	1.09
97	39/325	1.0	2.5	17.3	2.6	0.0	0.9	0.4	0.8	0.6	74.9	1.37
98	39/326	51.2	16.3	27.8	49.4	0.0	1.7	2.0	0.0	0.4	2.5	1.08
99	39/327	5.7	2.4	48.6	9.7	0.0	0.4	0.8	0.1	0.6	37.4	1.22
100	39/336	2.0	14.6	21.6	5.7	0.0	1.4	0.5	1.8	0.4	54.0	1.27
101	39/338	6.3	32.0	22.1	10.5	0.0	1.5	0.8	6.2	8.9	18.0	1.15
102	39/332	1.4	1.3	7.8	8.3	0.0	0.3	0.7	0.7	0.5	80.5	1.39
103	39/333	7.3	4.9	30.1	35.3	0.0	2.1	2.0	7.0	8.5	10.1	1.16
104	39/328	5.9	6.3	24.3	22.4	0.0	1.7	1.2	4.9	6.9	32.4	1.21
105	39/329	13.2	4.4	62.1	22.0	0.0	2.7	1.6	0.2	1.4	5.6	1.12
106	39/330	22.4	3.1	42.1	38.4	0.0	1.6	2.2	2.4	5.5	4.7	1.13
107	39/415	3.9	8.4	33.4	34.0	0.0	0.7	1.3	3.5	5.2	13.5	1.14
108	39/417	16.2	1.2	39.1	50.4	0.0	2.0	1.5	0.0	1.8	4.0	1.11
109	39/410	2.2	49.7	21.4	12.8	0.0	1.0	1.0	0.0	0.4	13.7	1.09
110	39/411	9.5	65.3	16.1	9.3	0.0	2.4	0.6	0.1	0.8	5.4	1.05
111	39/315	7.3	4.2	13.0	10.3	0.0	0.5	0.9	0.2	0.2	70.8	1.34
112	39/316	2.2	5.7	26.8	1.6	0.0	0.8	0.4	0.7	0.2	63.8	1.32
113	39/317	0.2	16.7	38.5	13.1	0.0	1.1	4.4	3.9	0.4	21.9	1.18
114	39/318	3.1	6.0	62.2	18.6	0.0	2.1	1.7	1.8	2.0	5.8	1.12
115	39/319	12.6	43.1	25.9	19.7	0.0	2.8	1.0	1.7	4.0	1.9	1.07
116	39/407	28.1	0.1	61.4	28.3	0.0	2.1	1.8	0.9	4.0	1.5	1.12
117	39/408	12.7	1.9	40.8	46.6	0.0	3.6	3.5	0.1	2.6	1.0	1.11
118	39/409	3.6	0.5	76.0	9.7	0.0	1.8	1.0	1.5	3.1	6.4	1.14

Table A2.8 continued.